

- **CARBONYL COMPOUND**
- **CARBOXYLIC ACID**
- **BIOMOLECULES AND POLYMER**

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*THEORY AND EXERCISE BOOKLET*

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## JEE SYLLABUS

### • CARBONYL COMPOUND

#### JEE - ADVANCED

Aldehydes and Ketones oxidation, reduction, oxime and hydrazone formation; aldol condensation, Perkin reaction; Cannizzaro reaction; haloform reaction and nucleophilic addition reactions (Grignard addition);

### • CARBOXYLIC ACID

#### JEE - ADVANCED

formation of esters, acid chlorides and amides, ester hydrolysis; Amines: basicity of substituted anilines and aliphatic amines, preparation from nitro compounds, reaction with nitrous acid,

### • BIOMOLECULES AND POLYMER

#### JEE - ADVANCED

Carbohydrates: Classification; mono- and di-saccharides (glucose and sucrose); Oxidation, reduction, glycoside formation and hydrolysis of sucrose.

Amino acids and peptides: General structure (only primary structure for peptides) and physical properties.

Properties and uses of some important polymers: Natural rubber, cellulose, nylon, teflon and PVC.

Practical organic chemistry: Detection of elements (N, S, halogens); Detection and identification of the following functional groups: hydroxyl (alcoholic and phenolic), carbonyl (aldehyde and ketone), carboxyl, amino and nitro; Chemical methods of separation of mono-functional organic compounds from binary mixtures.

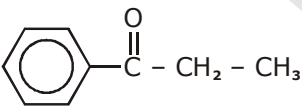
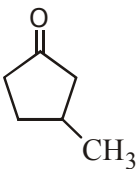
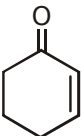
## CARBONYL COMPOUNDS

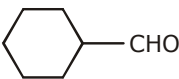
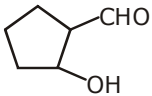
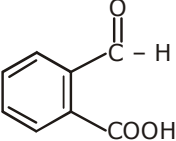
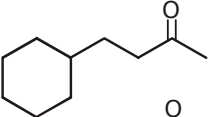
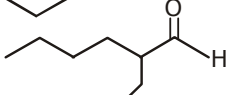
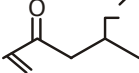

### 1. Introduction

These have general formula  $C_nH_{2n}O$  and contains  $>C=O$  group which is present in aldehyde  $\begin{matrix} R \\ \diagup \\ C=O \\ \diagdown \\ H \end{matrix}$

and  $\left[ \begin{matrix} R \\ \diagup \\ C=O \\ \diagdown \\ R \end{matrix} \right]$  ketone. Thus aldehydes and ketones are collectively called as carbonyl compounds

### 5. IUPAC Nomenclature of Aldehydes and Ketones

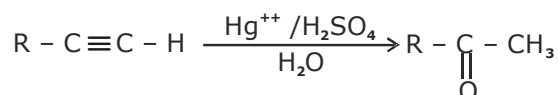
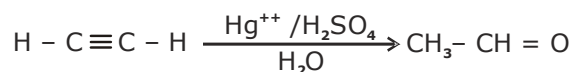
	Ketones	IUPAC name
1.	$CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_3$	Propanone
2.	$CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_2 - CH_3$	Butanone
3.	$CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_2 - CH_2 - CH_3$	Pentan-2-one
4.	$CH_3 - \overset{\overset{O}{\parallel}}{C} - \overset{\overset{O}{\parallel}}{C} - CH_3$	Butanedione
5.	$CH_3 - \overset{\overset{CH_3}{\mid}}{CH} - \overset{\overset{O}{\parallel}}{C} - \overset{\overset{CH_3}{\mid}}{CH} - CH_3$	2, 4-Dimethyl pentan-3-one
6.		1-Phenylpropan-1-one
7.		3-Methylcyclopentanone
8.		Cyclohex-2-en-1-one or 2-Cyclohexenone
9.	$CH_3 - \overset{\overset{O}{\parallel}}{C} - CH_2 - \overset{\overset{OH}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}} - CH_3$	4-Hydroxy-4-methyl pentan-2-one

	Ketones	IUPAC name
10.	$\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{H}$	Ethanol
11.	$\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{H}$	Propanol
12.	$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{H}_3$	Butanol
13.	$\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{H}$	3-Hydroxybutanal
14.	$\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH} - \text{CHO}$	Pent-2-en-1-el or Pen-2-enal
15.	$\text{CH}_2\text{CH}_2\text{CH}_2 - \underset{\text{Br}}{\text{CH}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{H}$	4-Bromo-3-methyl heptanal
16.		Cyclohexanecarbaldehyde
17.		2-Hydroxycyclopentane -1-carbaldehyde
18.	$\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_2 - \text{CHO}$	3-Oxopentanal
19.	$\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{CH}_2 - \text{COOH}$	3-Oxobutanoic acid
20.		2-Formylbenzoic acid
21.		2-(3-oxobutyl)-cyclohexanone
22.		2-ethylhex-2-en-1-al
23.		2,5-dimethylheptan-3-one
24.	$\text{CH}_3 - \underset{\text{Cl}}{\text{CH}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH} = \text{O}$	3-chloro-2-methylbutanal
25.		3-ethylcyclobutanone

## 8. General methods of preparation of Aldehyde and Ketones

### (I) Hydration of Alkyne :

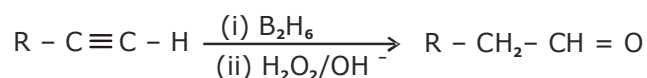
It is addition of water in the presence of heavy metal ion. acetylene on hydration gives aldehyde while any higher alkyne gives ketone.



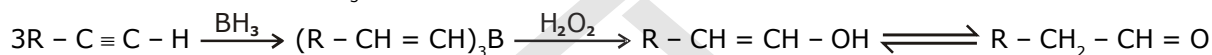
The preparation of carbonyl compounds from alkyne depends upon R part of (A) and also presence of inductive effect group attached to R.

### (II) Hydroboration of alkyne :

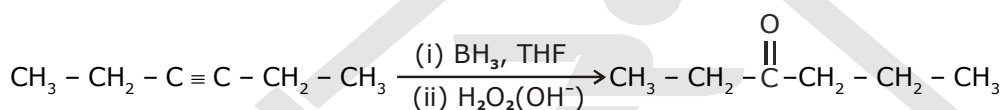
It is used to get aldehyde from alkyne-1. Here reagent is (i) diborane ( $\text{B}_2\text{H}_6$ ) (ii)  $\text{H}_2\text{O}_2(\text{OH}^-)$



In this reaction Borane ( $\text{BH}_3$ ) is electrophile.

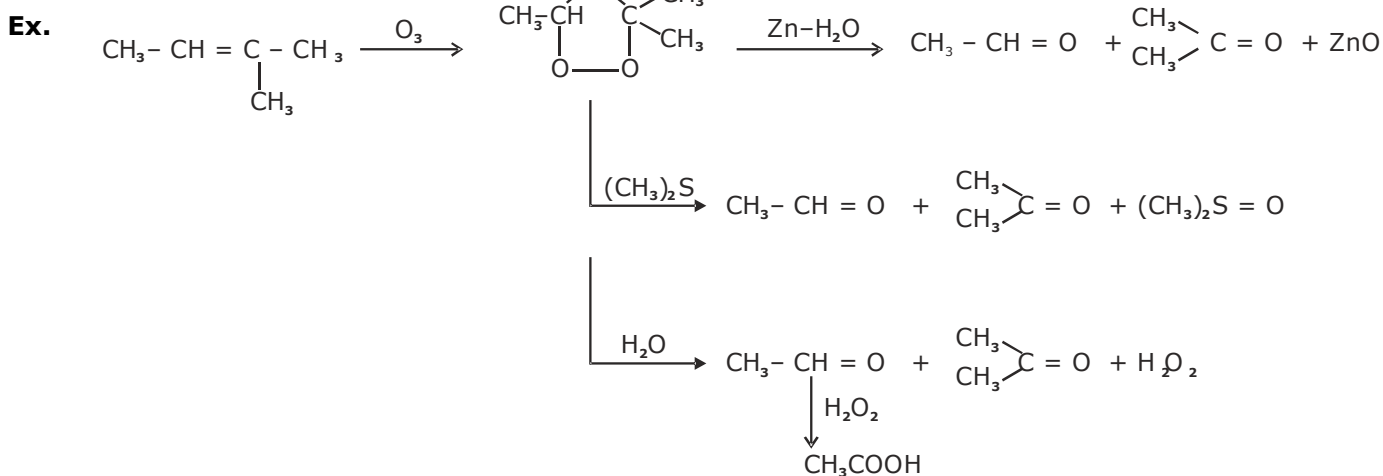
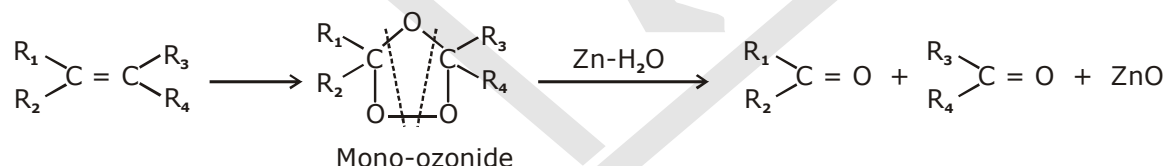


Higher alkyne except alkyne-1 will give ketone during hydroboration



### (III) Ozonolysis of alkene :

It is used to get carbonyl compounds from alkene. The reaction is



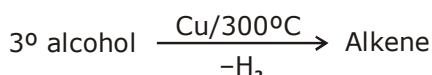
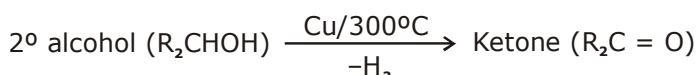
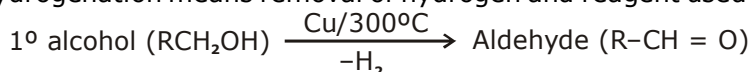
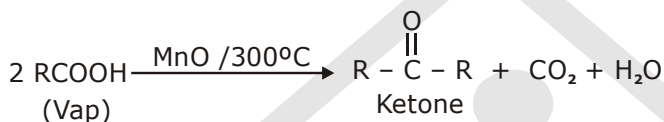
**Note :**

(I) During the cleavage of ozonide Zn is used to check further oxidation of aldehyde into acid.

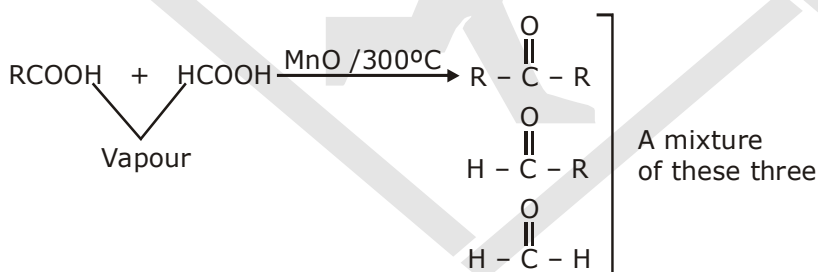
(II) By this method we can locate double bond in olefin or exact structure of hydrocarbon can be determined by knowing ozonolysis product i.e. by placing double bond at the place of two carbonyl oxygen of two carbonyl compounds.

**(V) Dehydrogenation of Alcohol :**

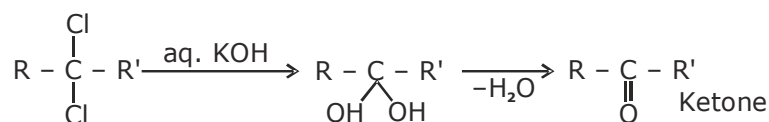
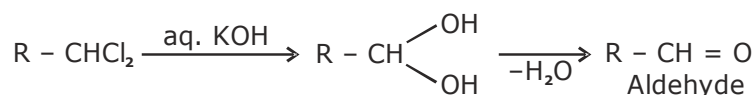
Dehydrogenation means removal of hydrogen and reagent used is heated copper.

**(VI) Dry distillation of Calcium salt of acid :****(VII) On passing vapours of fatty acids over Magnous oxide at 300°C.**

On passing mixture of vapours of fatty acid with formic acid we get a mixture of aldehyde, ketone and formaldehyde.

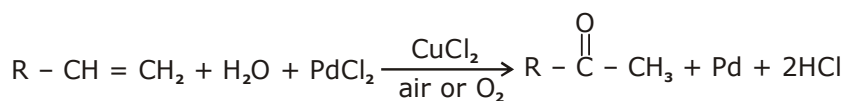
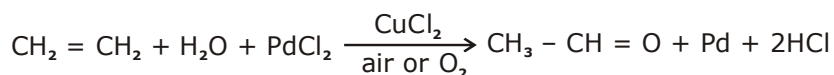
**(VIII) On aqueous alkali hydrolysis of gem-dihalides :**

Terminal gemdihalides will give aldehyde while non-terminal will give ketones as follows

**(IX) Wacker Process :**

Alkenes can directly be oxidised to corresponding aldehydes or ketone by treating them with a solution of  $\text{PdCl}_2$  containing a catalytic amount of  $\text{CuCl}_2$  in presence of air or  $\text{O}_2$ . Except ethene any higher alkene will give ketone.

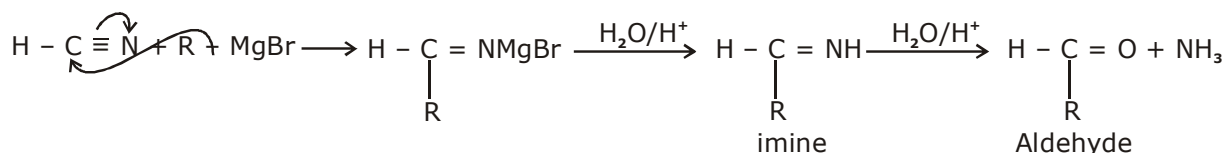




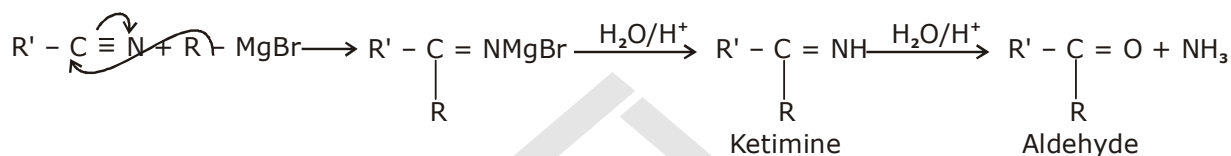
**Note :** During the reaction  $\text{PdCl}_2$  is reduced to Pd and  $\text{CuCl}_2$  is reduced to Cu(1)

**(X) Preparation of Carbonyl compounds using Grignard's Reagent :**

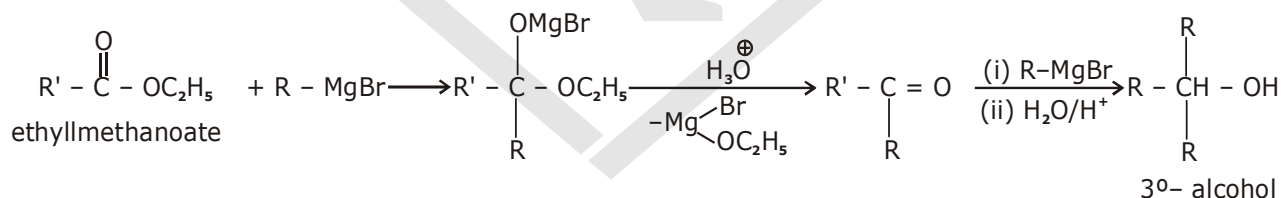
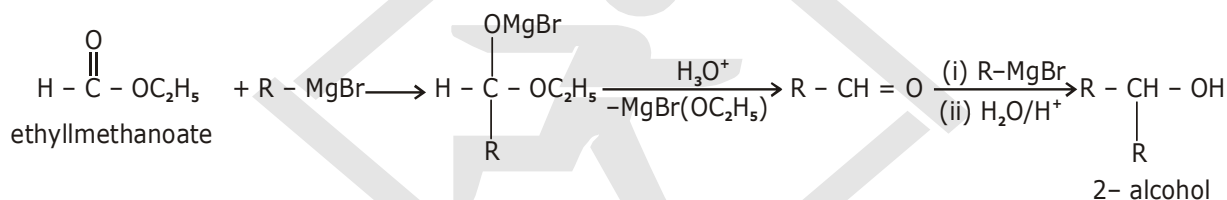
(a) Hydrogen cyanide on treating with Grignard reagent followed by double decomposition with water gives aldehyde via imine.



Alkylcyanide by using above process gives ketone via ketimine



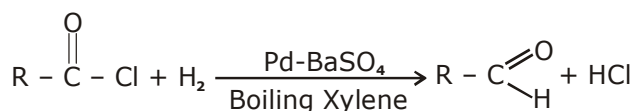
(b) Alkylformate with Grignard reagent gives 2° alcohol via aldehyde, while alkyl alkanoate under similar condition gives 3° alcohol via ketone



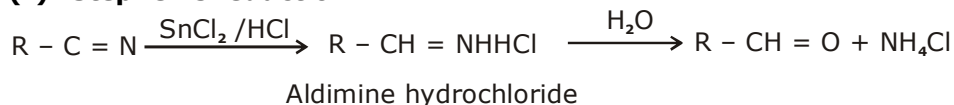
**(A) Methode used for the preparation of Aldehydes only.**

**(i) Rosenmund's reaction :**

Here acid chlorides are reduced to aldehyde with  $\text{H}_2$  in boiling xylene using palladium as a catalyst supported on barium sulphate.

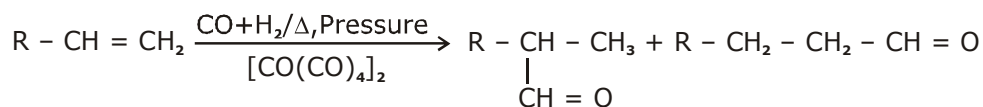


**(ii) Stephen's reduction :**

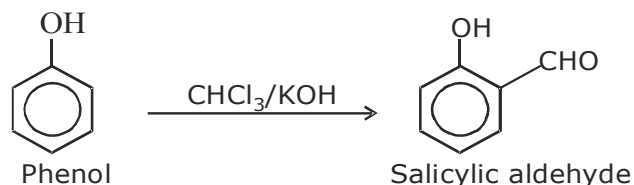
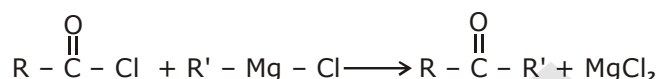
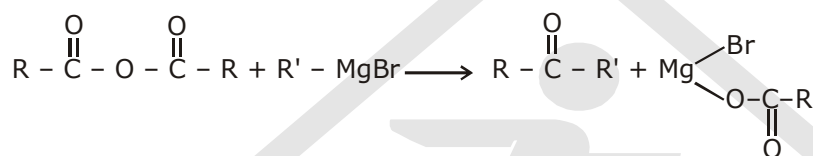
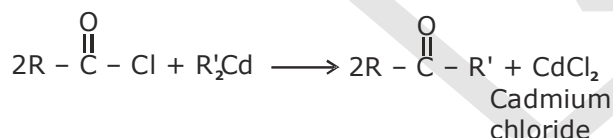
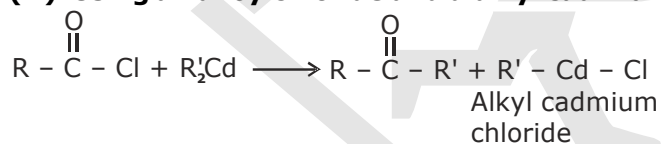
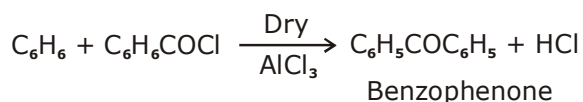
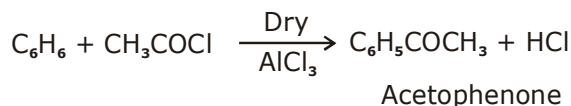
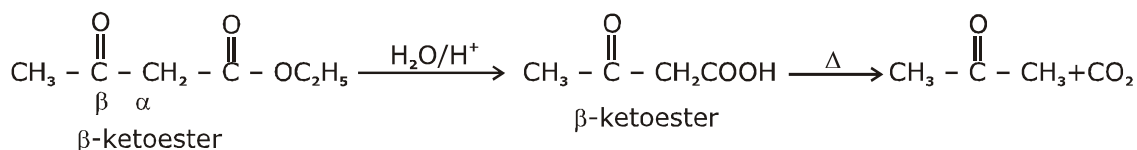


**(iii) Oxo-process :**

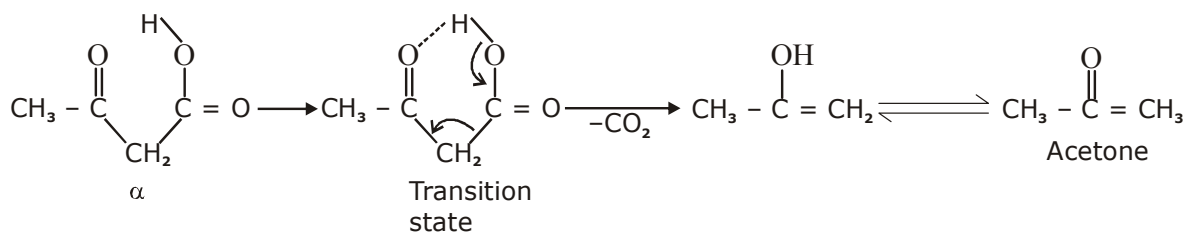
It is also called as carbonylation here alkene reacts with water gas at high temperature and pressure in the presence of cobalt carbonyl catalyst to give aldehyde.

**(iv) Reimer-Teimann Reaction :**

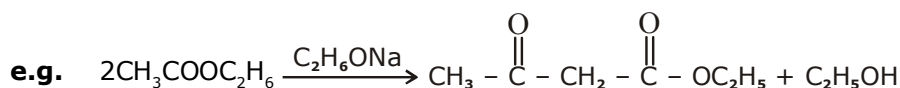
By this method phenolic aldehyde is prepared

**(B) Methods used for the preparation of Ketones only****(i) Using alkanoyl chloride and Grignard reagent****(ii) Using alkanoyl anhydride and Grignard reagent****(iii) Using alkanoyl chloride and dialkyl cadmium****(iv) By acylation or benzylation of aromatic hydrocarbon (Friedel-Crafts Reaction)****(v) By Acid hydrolysis followed by heating of  $\beta$ -Ketoester.**

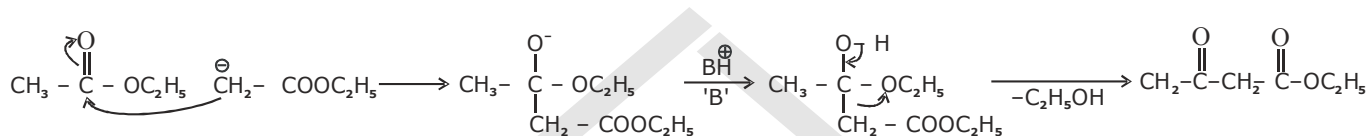
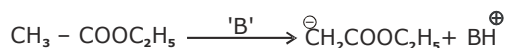
**Note : (i) It is  $\beta$ -ketoacid which decarboxylate more readily as it proceeds via six membered cyclic**



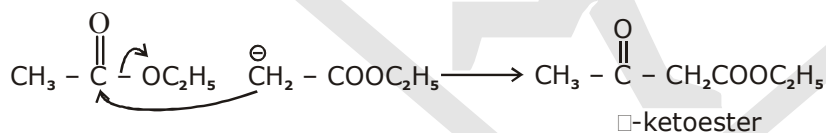
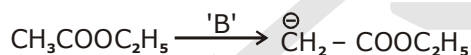
**Note : (ii)  $\beta$ -ketoester is obtained by claisen ester condensation of two moles of ester using sodium ethoxide as a base.**



**Mechanism :**

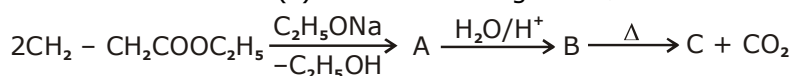


The product  $\beta$  ketoester can be easily obtained by placing anion of one ester at the place of ethoxy part of other ester as -

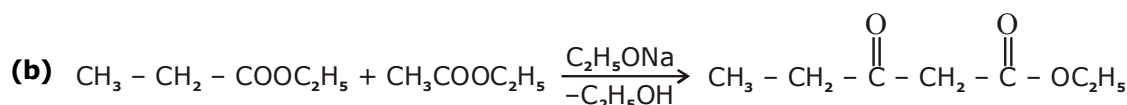
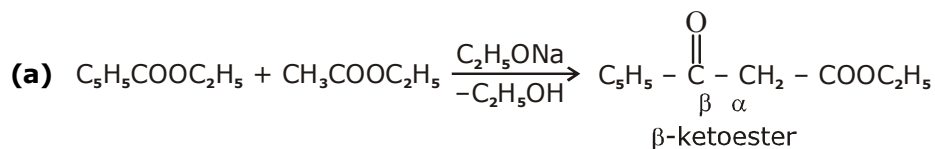


**Note : (iii) If two ester units are same then it is inter molecular claisen ester condensation**

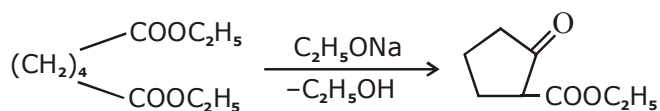
Q. Predict the unknown (s) for the following :



**Note : (iv) If two ester units are different then it is crossed Claisen ester condensation**



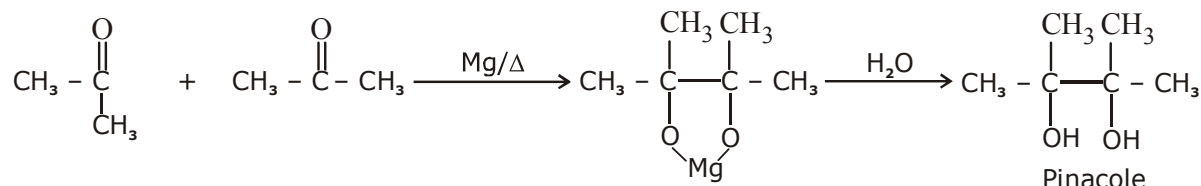
**Note : (v) If two ester units are present with in the same molecule then we get cyclic  $\beta$ -ketoester and the reaction is intramolecular Claisen ester condensation.**



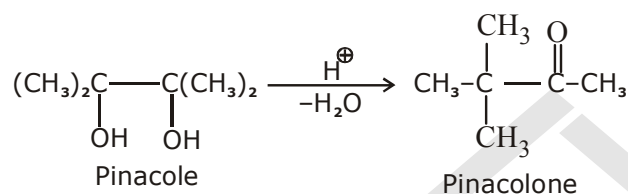
**Note : (vi) Active methylene group hydrogen is too acidic that it can be replaced by alkyl of arylalkyl halide in the presence of base like sodium ethoxide.**

### (C) Pinacol-Pinacolone rearrangement :

Pinacole is obtained when 2 moles of acetone are heated with divalent active metal magnesium followed by treating with water.



Pinacole undergoes rearrangement in acidic media to give pinacolone



## 9. Chemical Reactions of Carbonyl Compounds :

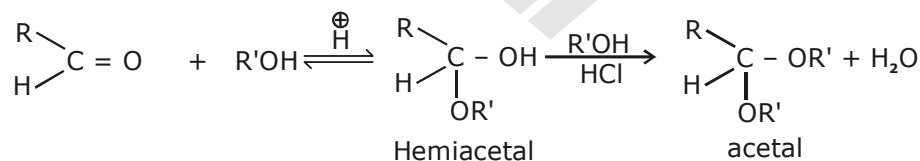
Carbonyl compounds undergo nucleophilic addition reaction and reactivity order will be :

### (I) Nucleophilic Addition Reaction :



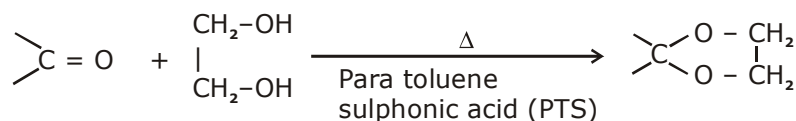
### (i) Reaction with alcohol :

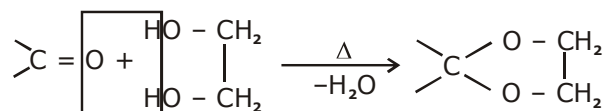
Carbonyl compounds react with alcohols in the presence of dry HCl gas to give acetal (if aldehyde) and ketal if ketone via formation of unstable hemiacetal and hemiketal respectively.



#### Note :

- (i) Acetal is formed to protect aldehyde for a long time.
- (ii) Acetal has functional groups ether.
- (iii) Acetal formed can be decomposed to original aldehyde by dilute acid.
- (iv) On treating with ethyleneglycol we get cyclic acetal or ketal (1, 3-dioxolans)

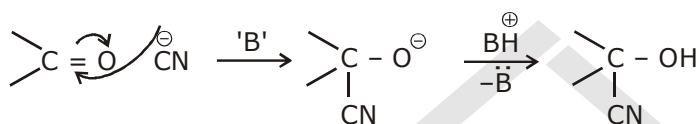
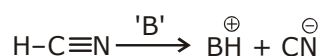
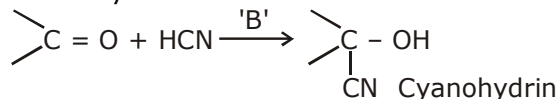


**Mechanism :**


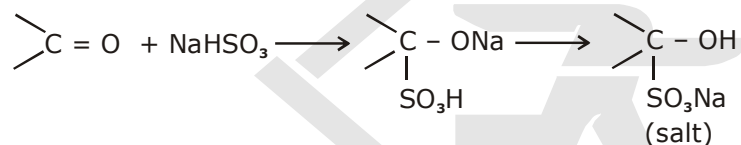
(v) Acetal formation is found to be more favourable than ketal formation. If both the carbonyl groups are present within the molecule.

**(ii) Addition of HCN :**

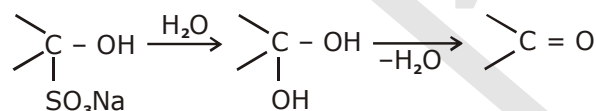
If is base catalysed addition


**(iii) Addition of sodiumbisulphite (NaHSO<sub>3</sub>) :**

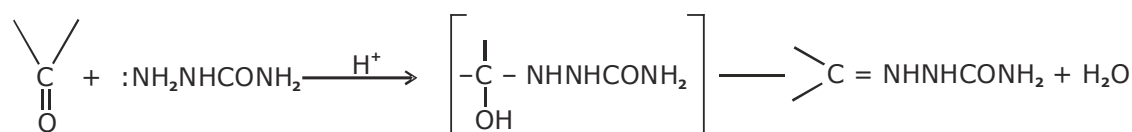
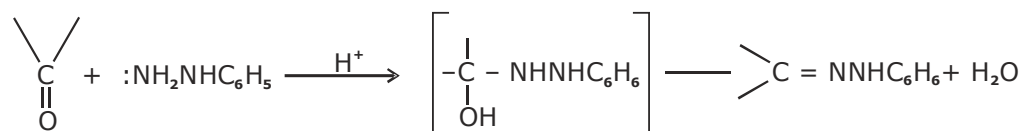
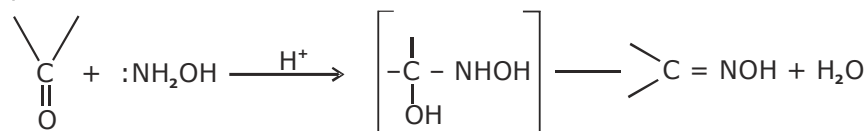
This addition is used to isolate carbonyl compounds from the mixture as we get salt.



Salt on acidification gives carbonyl compounds again.

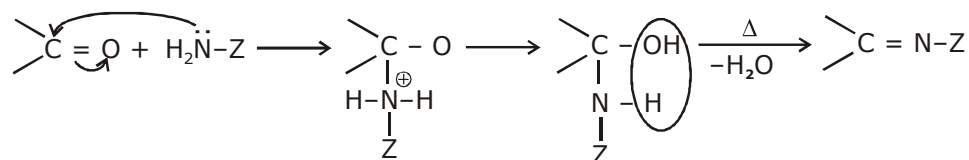
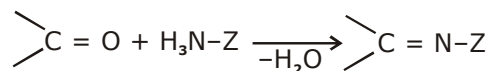

**(II) Addition elimination reactions :**

Certain compounds related to ammonia add to the carbonyl group to form derivatives that are important chiefly for the characterization and identification of aldehydes and , Ketones the product contain a carbon nitrogen double bond resulting from elimination of a molecule of water from the initial addition products.

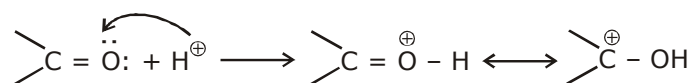


**(i) Reaction with ammonia derivatives ( $\text{H}_2\ddot{\text{N}}-\text{Z}$ ) :**

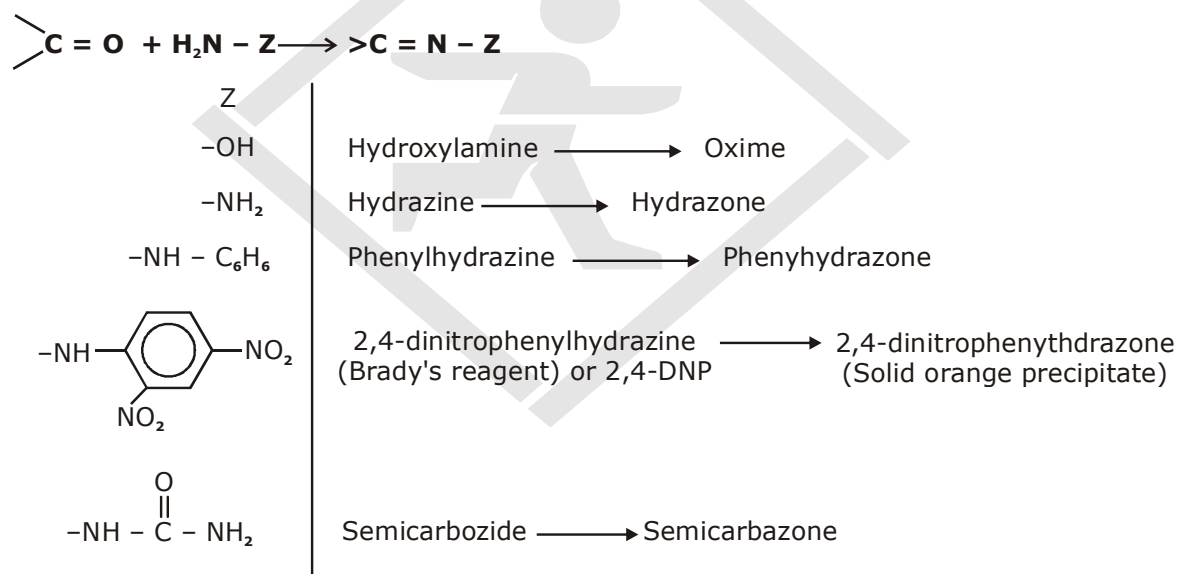
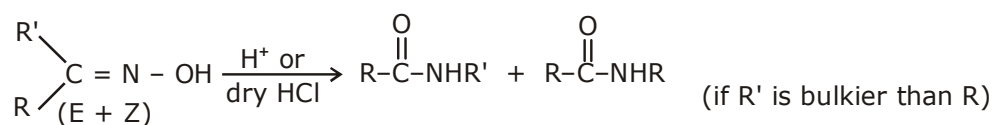
This reaction is nucleophilic followed by water elimination :



This reaction is carried out in slightly acidic media which will generate a nucleophilic centre for weak base ammonia derivatives.

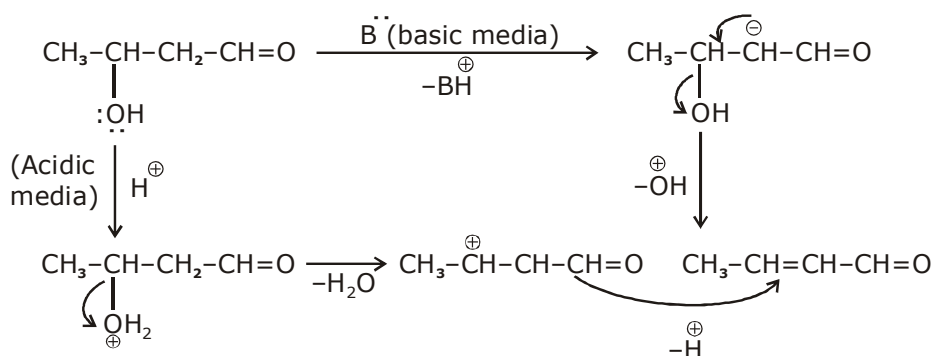


On using strong acidic media lone pair of electrons present at N-atom of ammonia derivatives will accept proton forming protonated ammonia derivatives which can not act as nucleophile for carbonyl carbon.

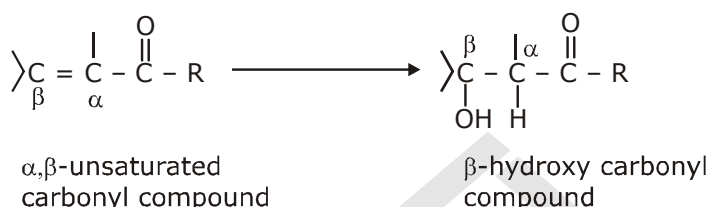
**(III) Beckmann Rearrangement in Oxime :**



from  $\beta$ -hydroxy aldehyde / ketone, water is eliminated on using either acidic or basic media as –



Now try to get carbonyl compounds from  $\alpha, \beta$ -unsaturated carbonyl compounds as – keep 'H' at  $\alpha$ -position and  $-\text{OH}$  at  $\beta$ -position of  $\alpha, \beta$  unsaturated carbonyl compounds to get  $\beta$ -hydroxy carbonyl compounds.

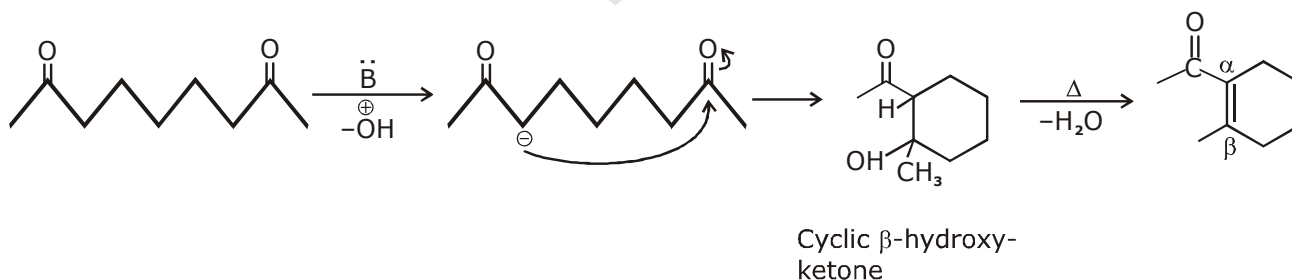


Now break  $\alpha$  and  $\beta$  carbon as shown below to get carbonyl compound.



These two carbonyl compounds can be obtained on ozonolysis of hydrocarbon  $\text{>C}=\underset{\text{R}}{\text{C}} + \text{CH}_2$  if it is asked.

### Intramolecular aldol condensation :

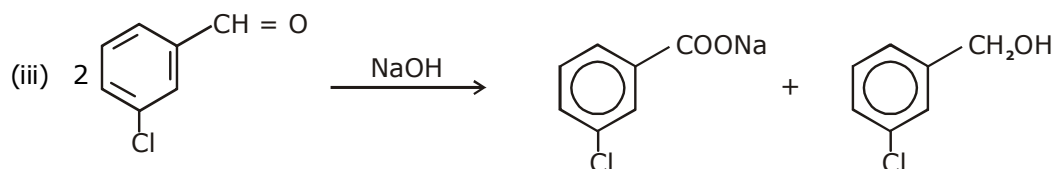
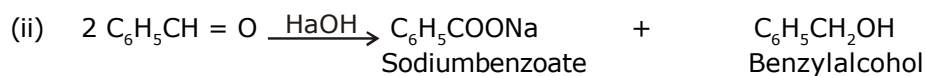
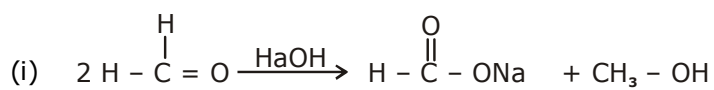


By knowing product we can get reactant as in case of intermolecular aldol condensation :

### (V) Cannizzaro reaction :

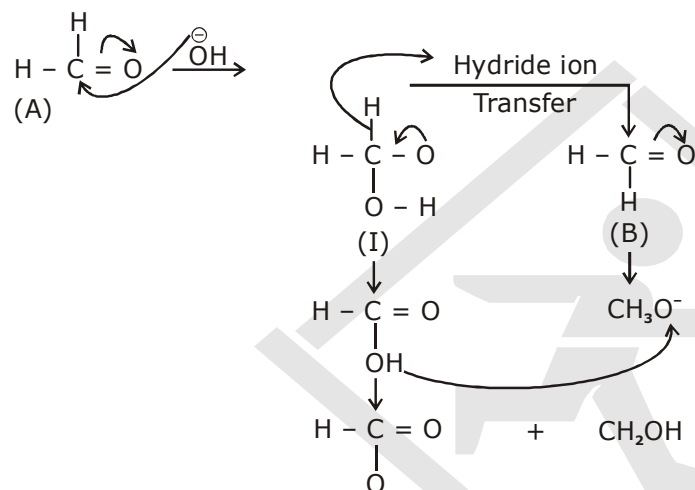
Carbonyl compounds not having  $\alpha$ -hydrogen atom undergo disproportionation or redox reaction in strong basic media.





These reaction are intermolecular cannizzaro reaction :

### Mechanism :

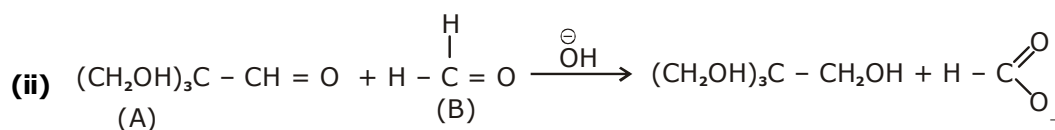
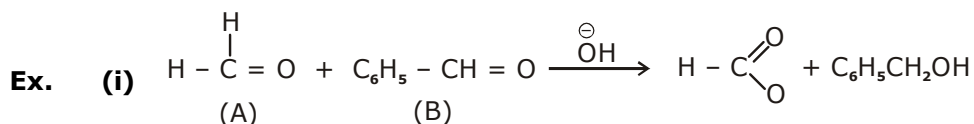


By this mechanism it clear that acid is corresponding to that carbonyl compound over which OH is going easily as nucleophile.

**Note :** It is observed that hydride ion transfer from (I) to Carbonyl compound (B) is rate determining step.

### Crossed Cannizzaro reaction :

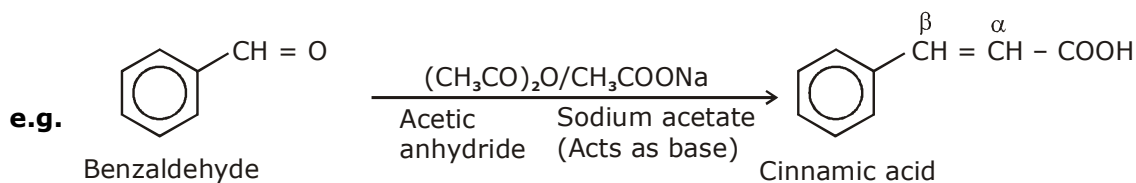
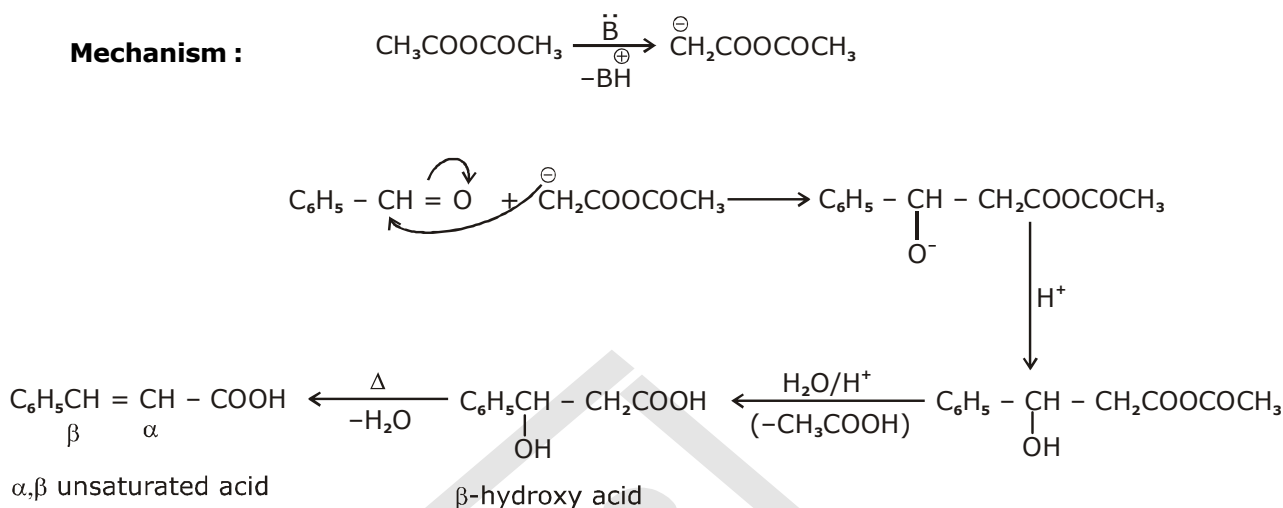
On using two types of carbonyl compounds not having  $\alpha$ -hydrogen atom, acid will be corresponding to that aldehyde over which OH will approach without any hindrance.



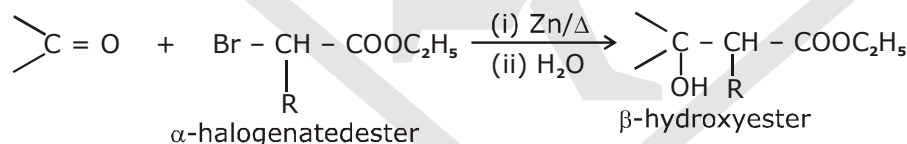
in case (i) OH will easily go to (A) and in case (ii) it will go to (B) hence acid will be formate ion in both the cases.

**(VI) Perkin reaction :**

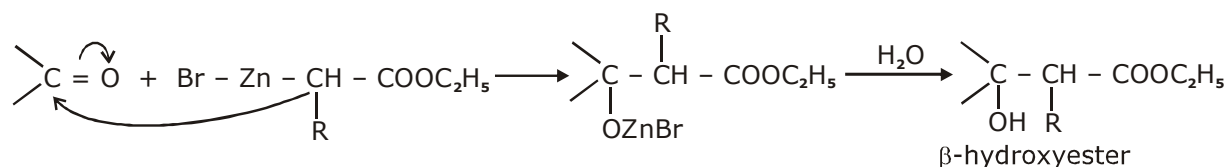
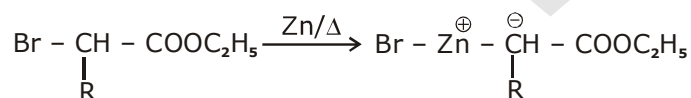
When aromatic aldehyde like benzaldehyde is treated with anhydride in the presence of sodium salt of acid from which anhydride is derived we get  $\alpha,\beta$ -unsaturated acid.

**Mechanism :****(VII) Reformatsky reaction :**

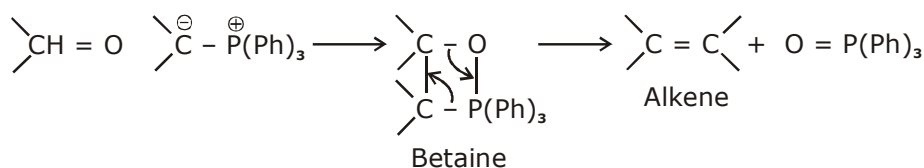
When carbonyl compound and  $\alpha$ -halogenated ester are heated with zinc followed by treating with water we get  $\beta$ -hydroxyester.



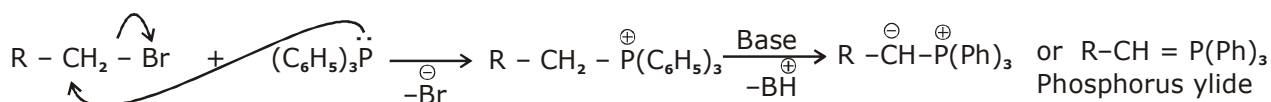
This reaction can be represented as -

**(VIII) Wittig reaction :**

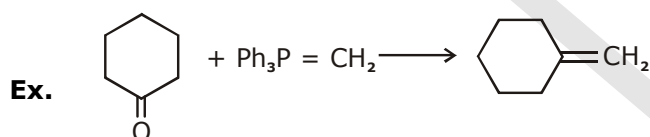
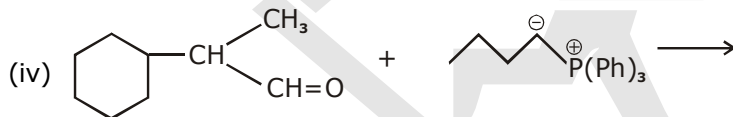
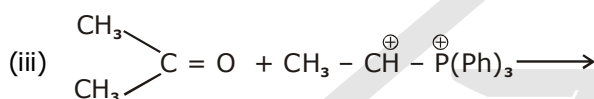
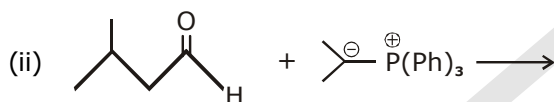
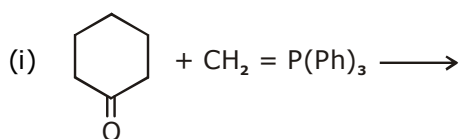
It is used to get alkene from carbonyl compound using phosphorus ylide via the formation of cyclic structure betaine.



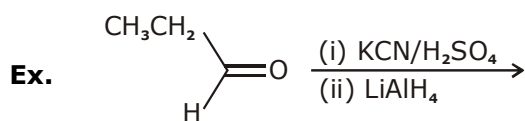
**Note :** Phosphorus ylides are prepared from alkylhalide and triphenylphosphine in the presence of base like sodium ethoxide as –



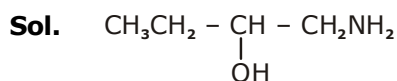
Q. Predict the product for the following :



[JEE-96]

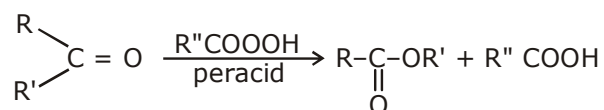


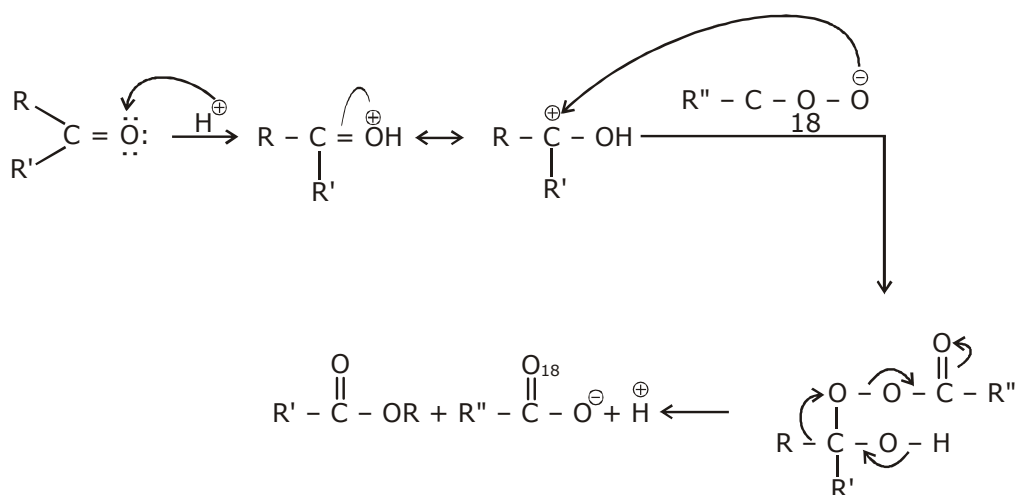
[JEE-96]



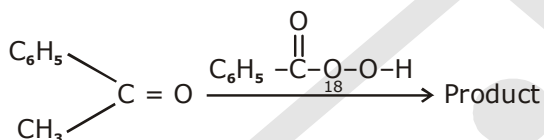
### (IX) Baeyer-Villiger oxidation :

It is preparation of ester from ketone using peracid.

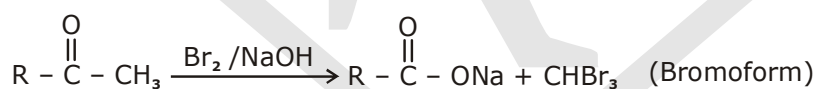


**Mechanism :**

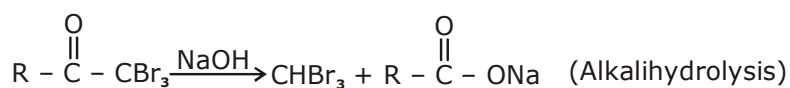
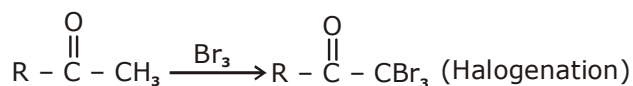
Q. Predict product for the following

**(X) Haloform reaction :**

Acetaldehyde and methylalkyl ketones react rapidly with halogen ( $\text{Cl}_2$ ,  $\text{Br}_2$  or  $\text{I}_2$ ) in the presence of alkali to give haloform and acid salt.



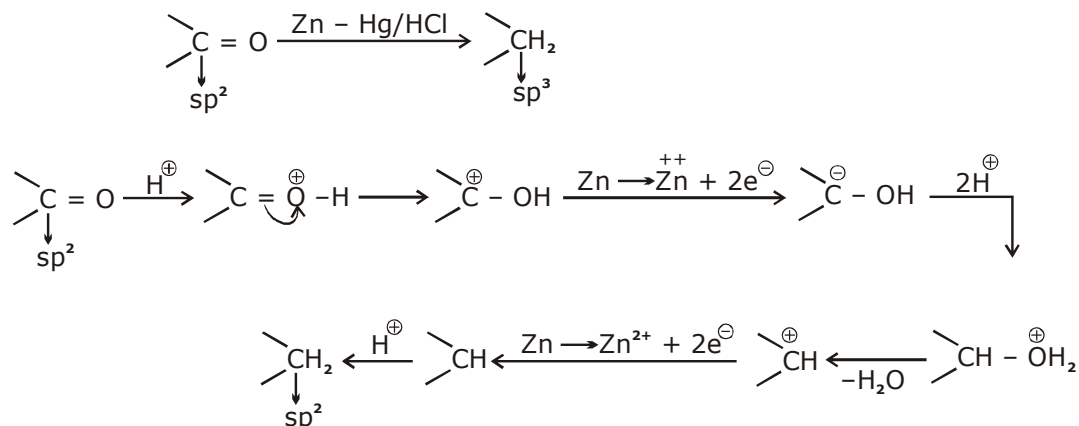
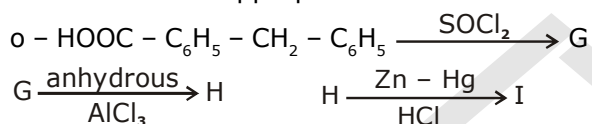
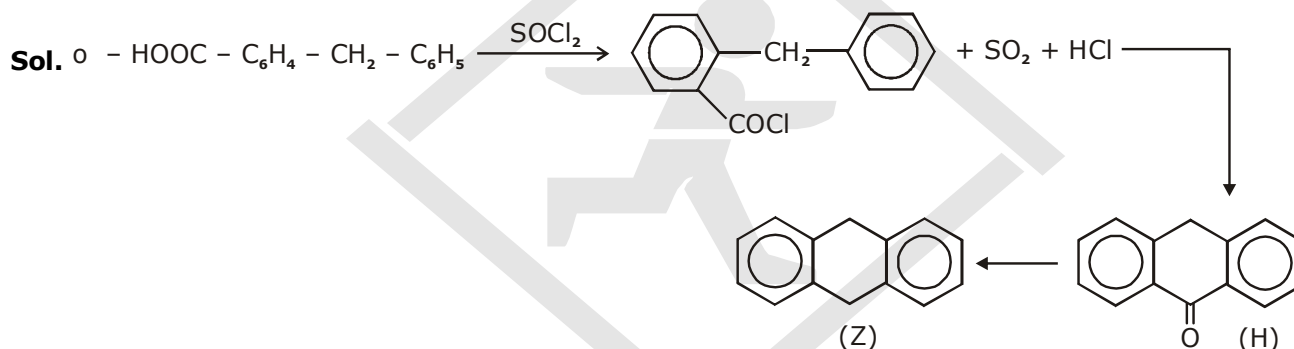
In this reaction  $-\text{CH}_3$  of  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$  group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone gives acid salt having carbon atom corresponding to alkyl ketone.

**(a) Halogenation****(b) Alkali hydrolysis**

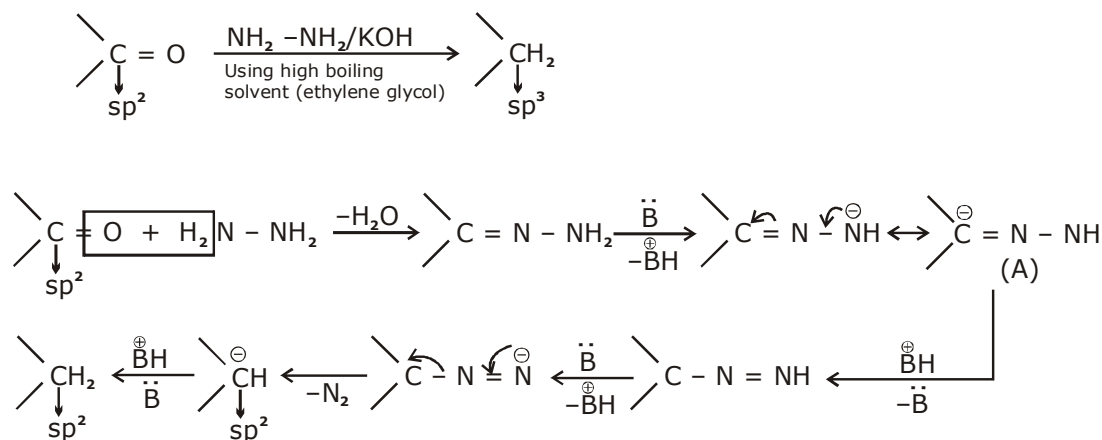
**Note :** This reaction is used to distinguish the presence of  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$  group.

**(XI) Clemmensen reduction :**

Used to get alkane from carbonyl compounds.

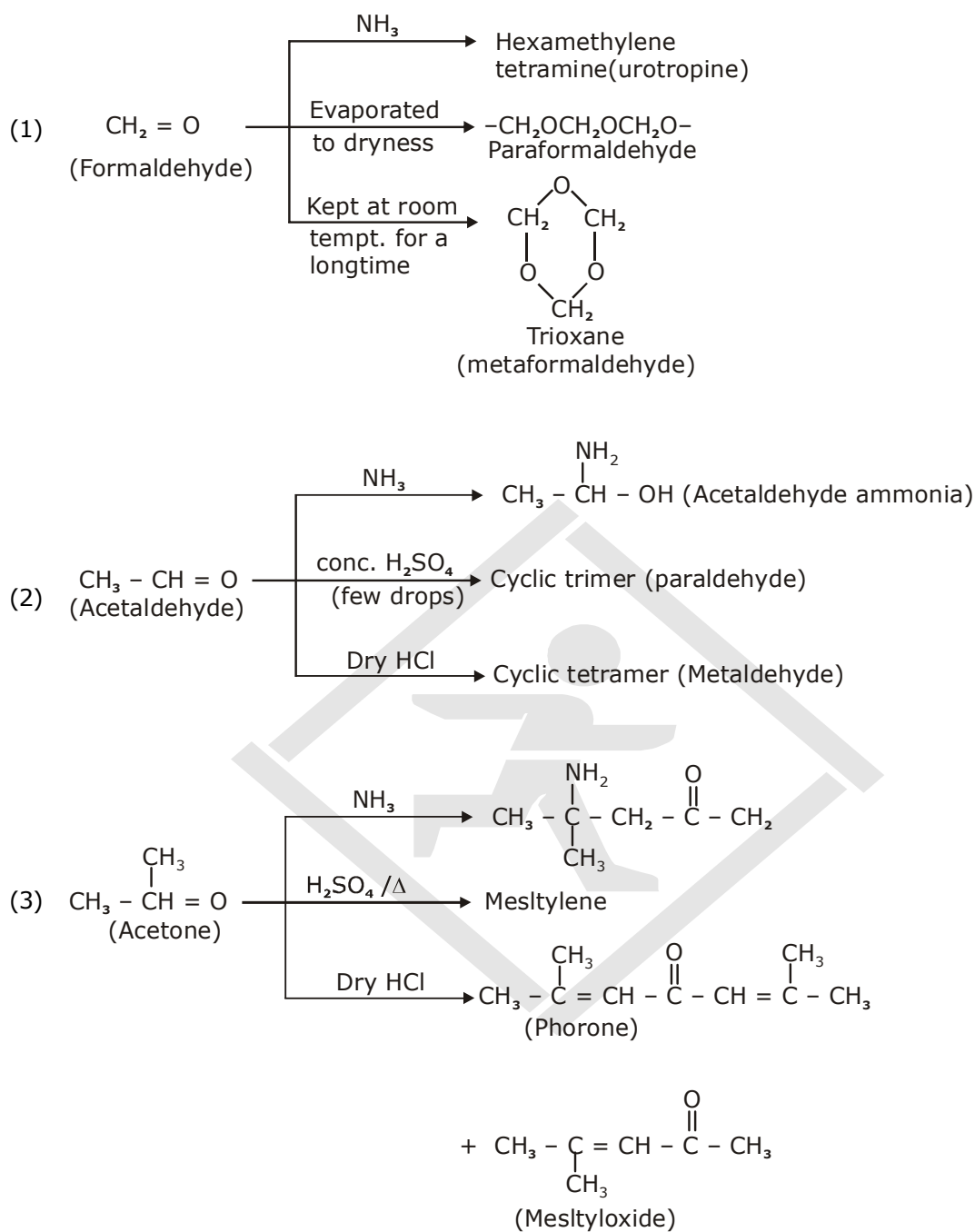

**Ex.** Fill in the blanks with appropriate structures of reaction products in the following transformations

**[JEE-95]**

**(XII) Wolf-Kishner reduction :**

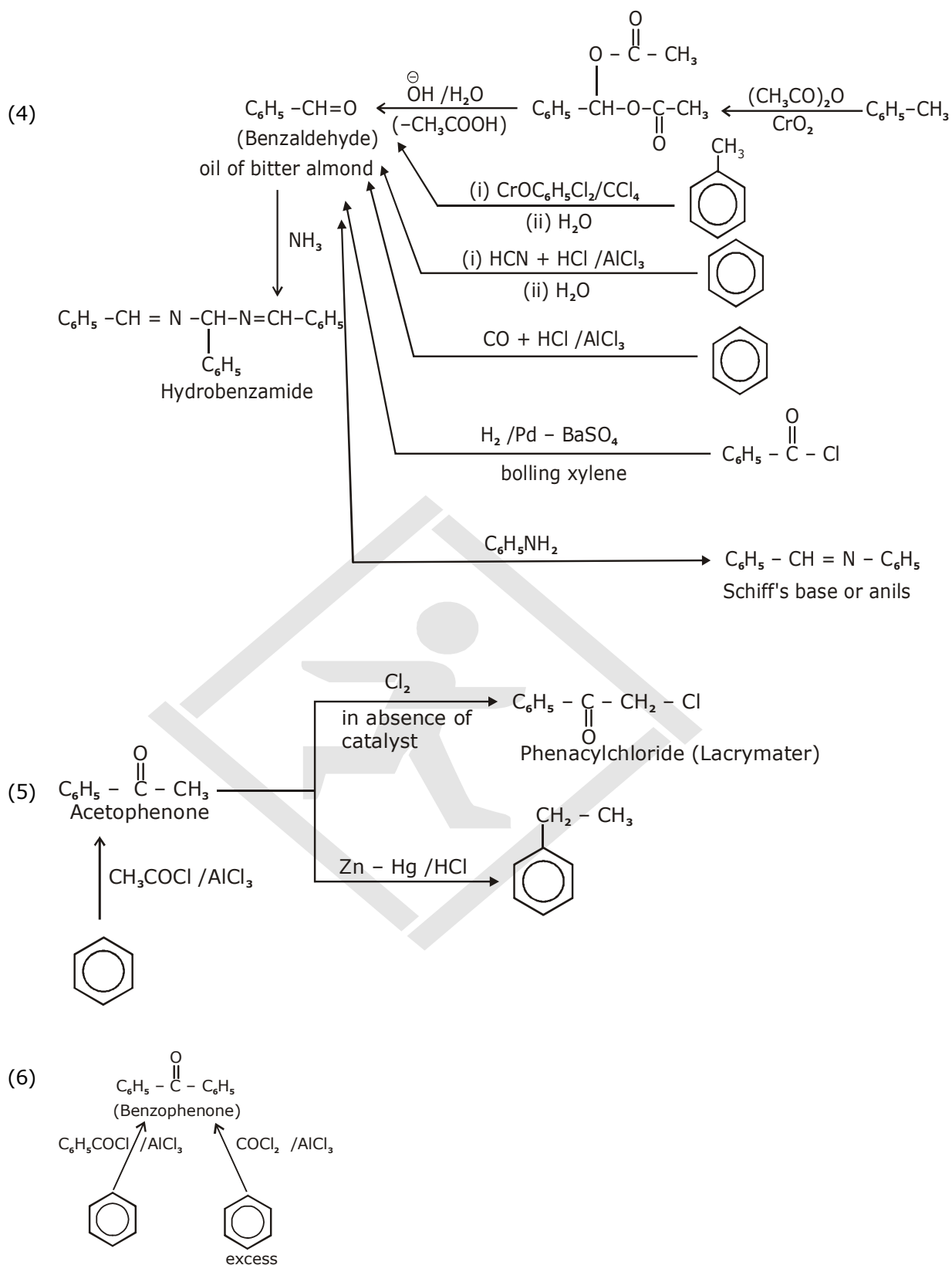
(Used to get alkane from carbonyl compounds)





## Other reaction :

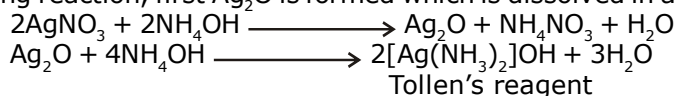




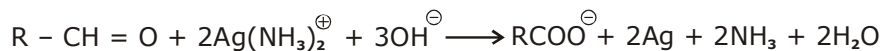


**Some important reagents used for identification of aldehyde.****(i) Tollen's reagent :**

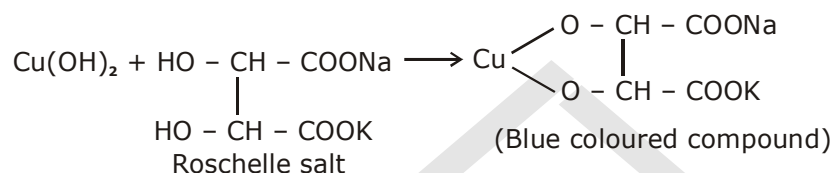
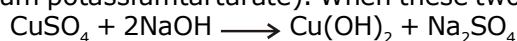
It is ammoniacal silver nitrate solution, prepared by adding ammonium hydroxide to  $\text{AgNO}_3$  solution. During reaction, first  $\text{Ag}_2\text{O}$  is formed which is dissolved in ammoniumhydroxide to give Tollen's reagent.



Tollen's reagent is weak oxidising agent, it gives Ag mirror test with aldehyde.

**(ii) Fehling's solution :**

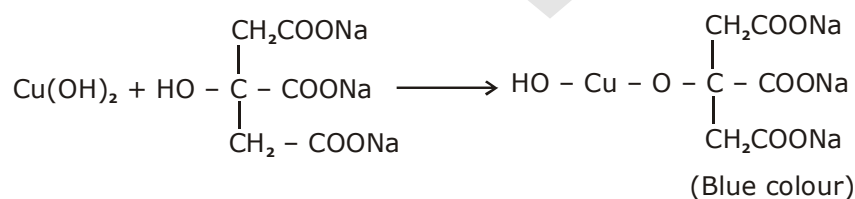
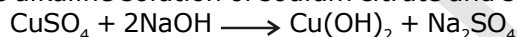
It is an alkaline solution of cupric ion complexed with sodium potassium tartarate. Two solutions are kept by naming Fehling solution (I) ( $\text{CuSO}_4$  solution) and Fehling solution (II) (Alkaline solution of sodium potassiumtartarate). When these two solutions are mixed we get deep blue coloured solution.



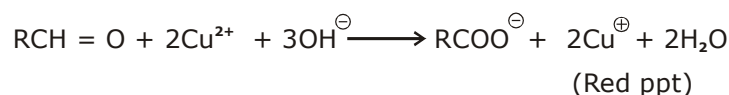
Equal volume of both the solution are heated with aldehyde to give red brown precipitate of cuprous oxide ( $\text{Cu}_2\text{O}$ ) which confirms the presence of aldehyde.

**(iii) Banadict solution :**

It is solution of  $\text{CuSO}_4$ , sodium citrate and sodium carbonate. It also consists of two solution. Solution (I) is alkaline solution of sodium citrate and solution (II) is  $\text{CuSO}_4$  solution.



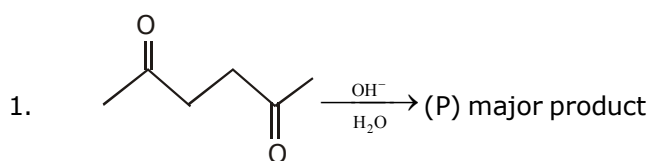
Aldehyde gives positive test with Benedict solution.

**(iv) Schiff's reagent :**

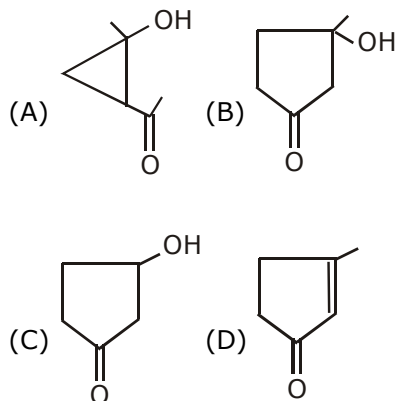
It is dilute solution of rossniline hydrochloride whose red colour has been discharged by passing  $\text{SO}_2$ . Aldehyde reatores red colour when treated with schiff's reagent (Magenta solution in  $\text{H}_2\text{SO}_4$ ).

## Exercise - I

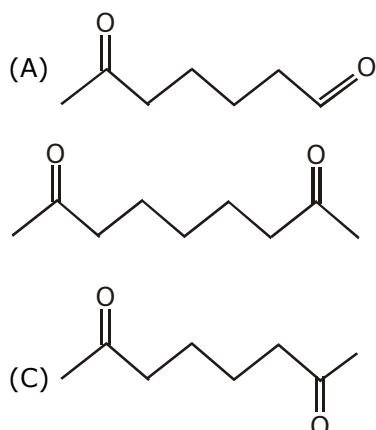
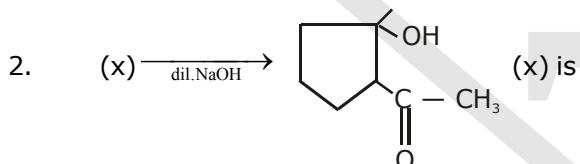
(Only one option is correct)



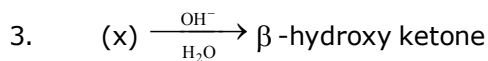
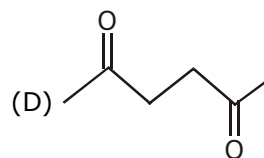
Structure of (P) is



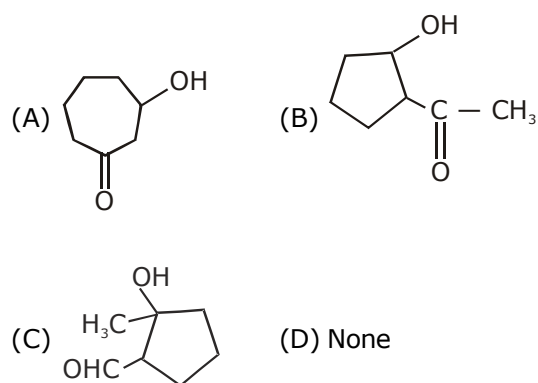
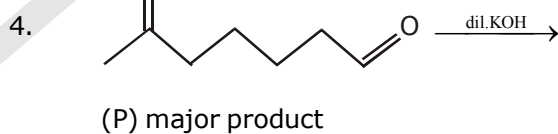
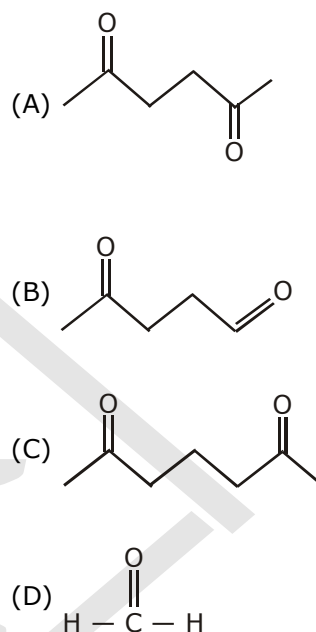
Sol.




( B )

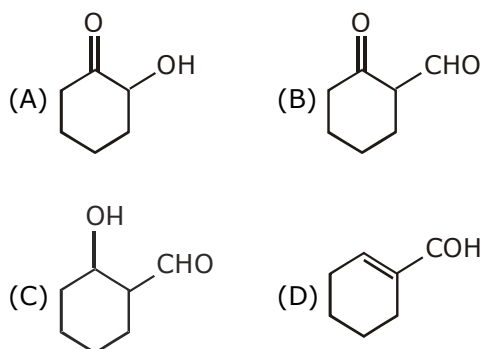


(x) can't be



Sol.

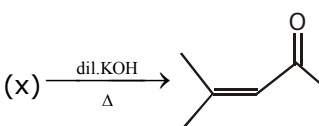
5.  major product structure of (x) is

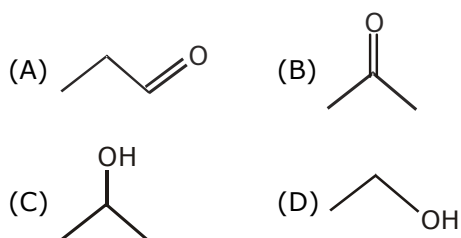


Sol.

6. Aldol addition can be  
 (A) Acid catalysed (B) Base catalysed  
 (C) Acid promoted (D) A and B both

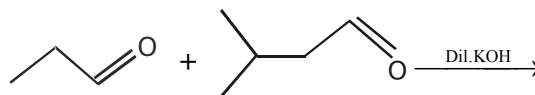
Sol.

7.  Structure of (x) is



Sol.

8.

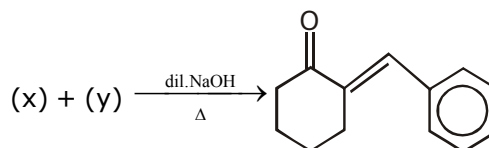


Total number of aldol condensation products are (excluding stereoisomer)

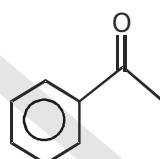
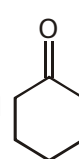
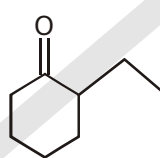
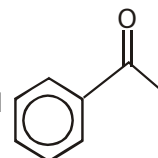
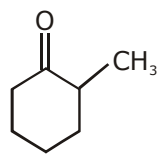
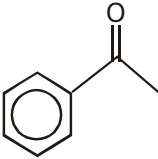
- (A) 2 (B) 3  
 (C) 4 (D) 5

Sol.

9.

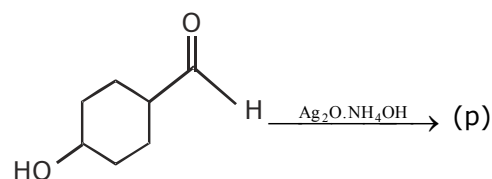


(x) and (y) are

- (A)  and   
 (B)  and   
 (C)  and   
 (D) None

Sol.

10.

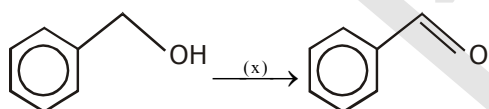


Product (P) is

- (A)
- (B)
- (C)
- (D)

**Sol.**

11.

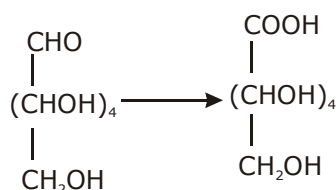


Reagent (x) is

- (A) PCC (B)  $\text{CrO}_3, \text{H}_2\text{SO}_4, \text{H}_2\text{O}$   
(C)  $\text{Ag}_2\text{O}, \text{NH}_4\text{OH}$  (D) All

**Sol.**

12.



Reagent responsible for given conversion will be

- (A)  $\text{Ag}_2\text{O}, \text{NH}_4\text{OH}$  (B)  $\text{Br}_2, \text{H}_2\text{O}$   
(C)  $\text{Cu}^{+2}$  (D) All

**Sol.**

13.  $\text{HCHO} \xrightarrow{\text{Conc. NaOH}} (\text{x}) + (\text{y})$

(i) Oxidation number of carbon changes from

- (A) 0 to +1 and 0 to -2  
(B) 0 to +1 and 0 to -1  
(C) 0 to +2 and 0 to -2  
(D) None

(ii) Given reaction is an example of

- (A) oxidation (B) Reductopn  
(C) both (D) None

**Sol.**

14. Compound which gives cannizaro reaction?

- (A)  $\text{CD}_3\text{CHO}$  (B)  $\text{C}_6\text{H}_5\text{CHO}$   
(C)  $\text{CH}_3\text{COCH}_3$  (D)

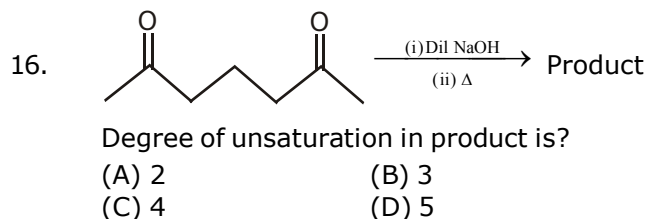
**Sol.**

15. Compound which gives intramolecular aldol re-action?

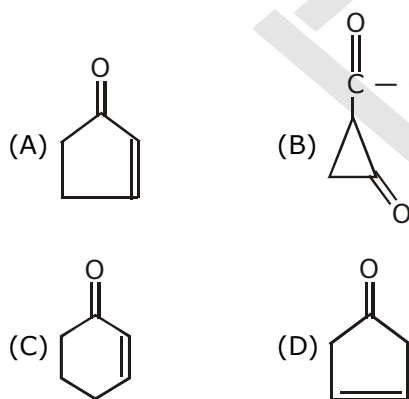
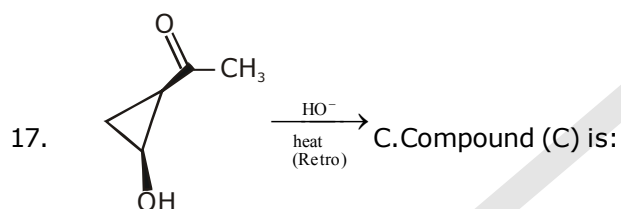
- (A)
- (B)
- (C)

(D) B and C both

Sol.

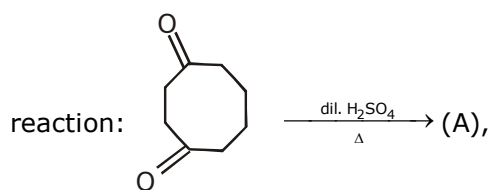


Sol.

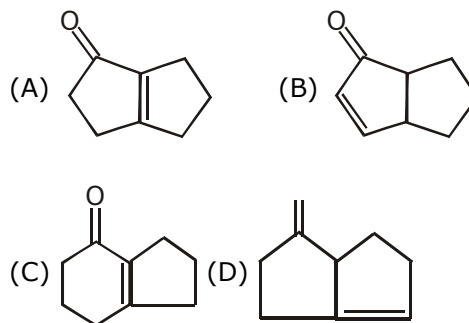


Sol.

18. This is an example of an intramolecular aldol



Product (A) is:



Sol.

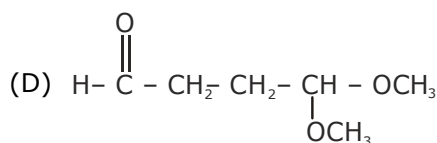
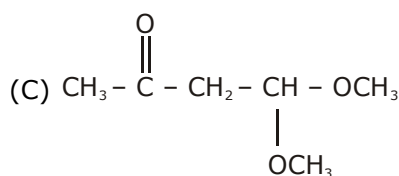
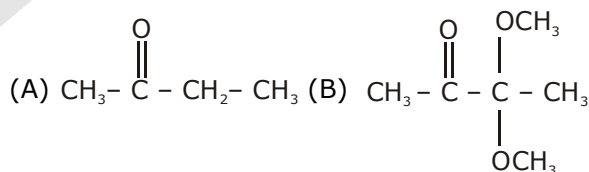
19. Which acid can be oxidised by Fehling solution:

- (A) Malonic acid (B) Acetic acid  
(C) Oxalic acid (D) formic acid

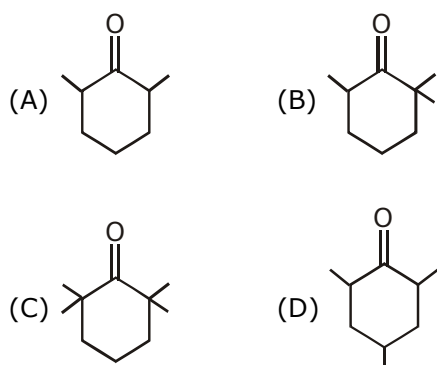
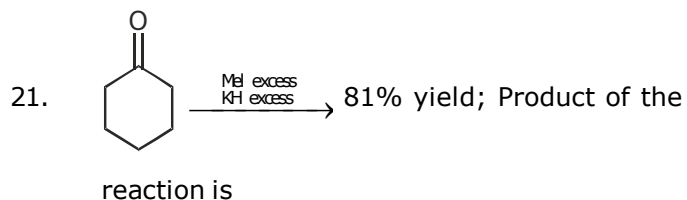
Sol.



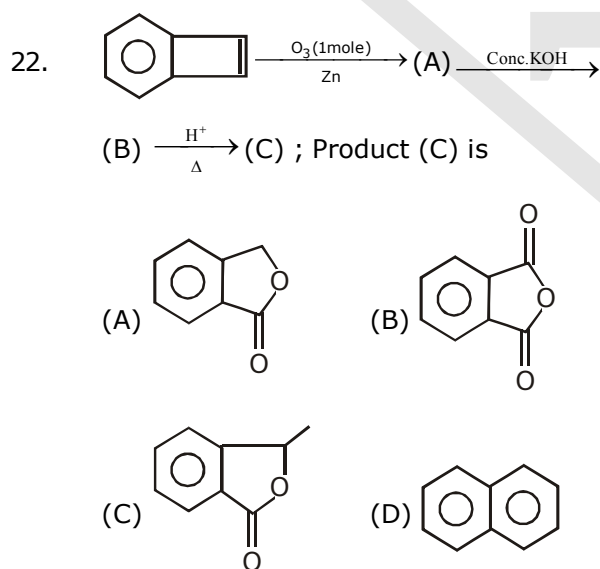
Positive Tollen's Test Compound (A) is :



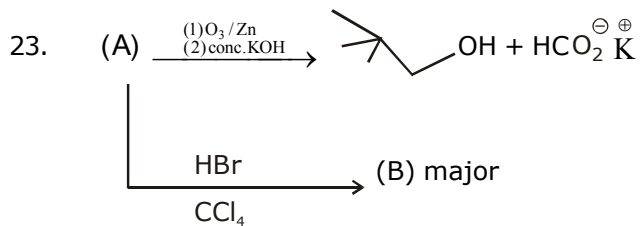
Sol.



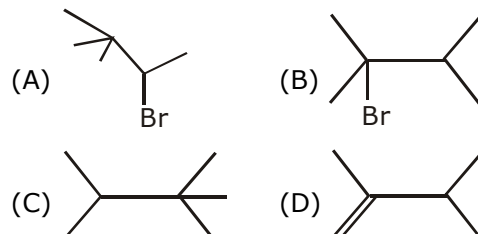
Sol.



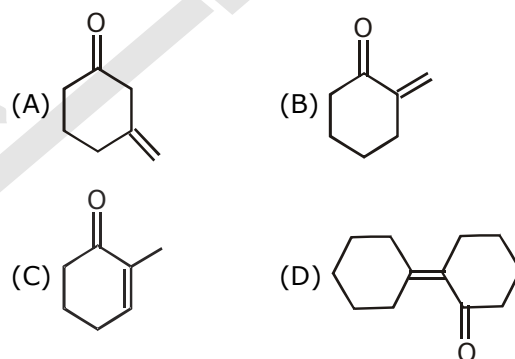
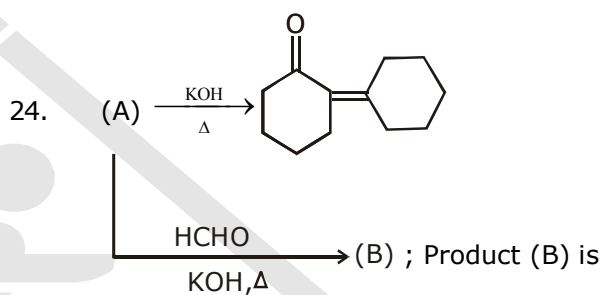
Sol.



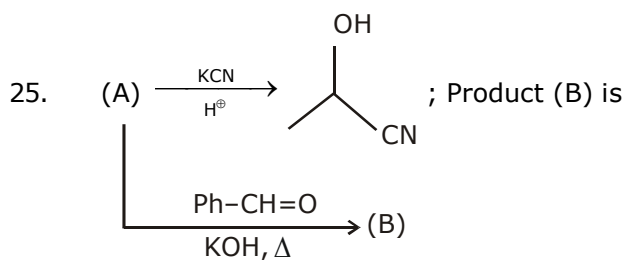
Product (B) is



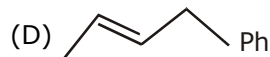
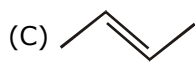
Sol.



Sol.

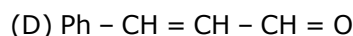
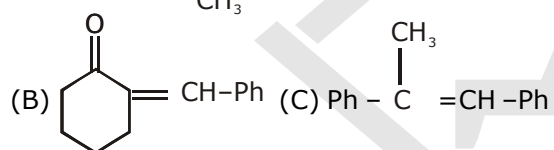
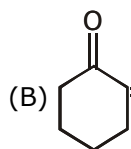
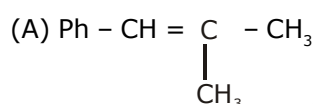
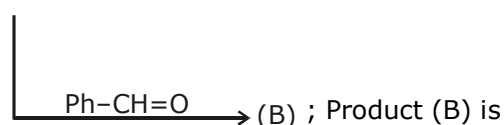


- (A)  $\text{Ph} - \text{CH} = \text{CH} - \text{Ph}$   
 (B)  $\text{Ph} - \text{CH} = \text{CH} - \text{CH} = \text{O}$



**Sol.**

26. (A)  $\xrightarrow[\text{tollen's test}]{\text{Positive}}$

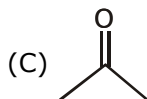
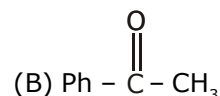
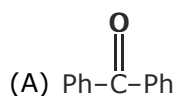


**Sol.**

27. Gem dihalide on hydrolysis gives:  
 (A) Vic diol (B) Gem diol  
 (C) Carbonyl compound  
 (D) Carboxylic acid

**Sol.**

28.  $\text{Ph} - \text{CO}_2\text{H} + \text{CH}_3\text{CO}_2\text{H}$



(D) All

**Sol.**

29. Arrange these compounds in decreasing order of reactivity for the nucleophilic addition reaction:

- (I) Acid chloride (II) Aldehyde  
 (III) Ketone (IV) Ester

Select the correct answer from the codes given below:

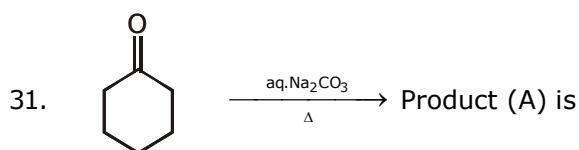
- (A)  $\text{I} > \text{II} > \text{III} > \text{IV}$  (B)  $\text{IV} > \text{III} > \text{II} > \text{I}$   
 (C)  $\text{III} > \text{II} > \text{I} > \text{IV}$  (D)  $\text{I} > \text{IV} > \text{II} > \text{III}$

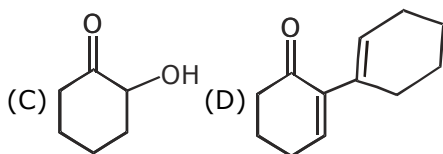
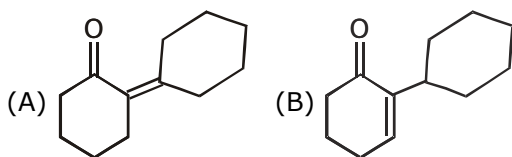
**Sol.**

30. Acetal or ketal is:

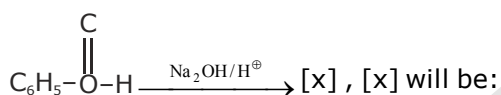
- (A) Vic dialkoxy compound  
 (B)  $\alpha, \omega$ -dialkoxy compound  
 (C)  $\alpha$ -alkoxy alcohol  
 (D) Gem dialkoxy compound

**Sol.**



**Sol.**

32. In the given reaction:



- (A) Only syn oxime  
(B) Only anti oxime  
(C) Mixture of syn and anti oxime  
(D) Secondary amide

**Sol.**

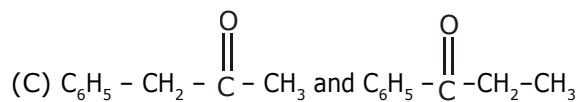
33. Schiff's base is prepared from:

- (A) Carbonyl compound and primary amine  
(B) Carbonyl compound and secondary amine  
(C) Carbonyl compound and tertiary amine  
(D) All of these

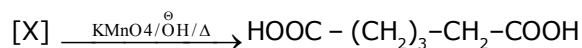
**Sol.**

34. Schiff's reagent is used for the differentiation between:

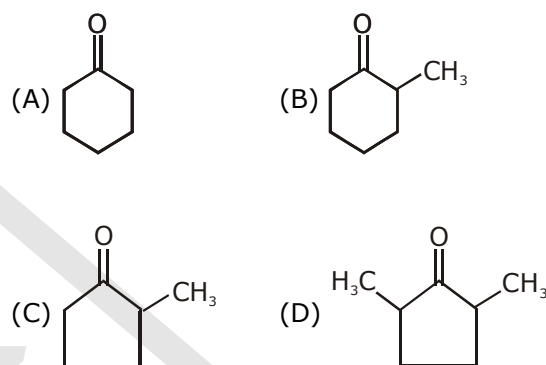
- (A) HCHO and  $\text{CH}_3\text{CHO}$   
(B)  $\text{CH}_3\text{COCH}_3$  and  $\text{CH}_3\text{CHO}$

(D) HCHO and  $\text{C}_6\text{H}_5\text{CHO}$ **Sol.**

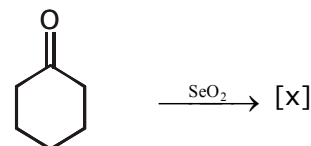
35. In the reaction sequence [X] is ketone:



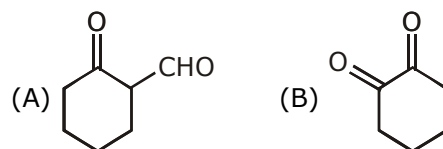
[X] will be:

**Sol.**

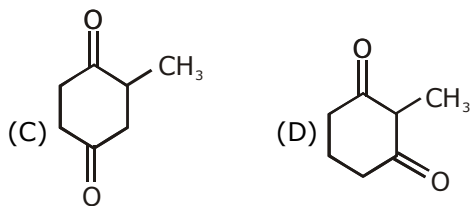
36. In the given reaction



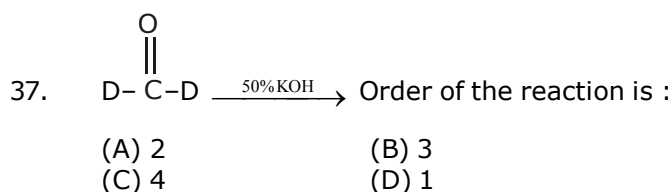
[X] will be :





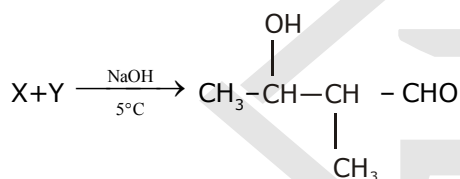


**Sol.**



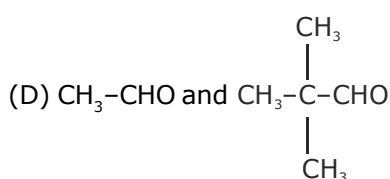
**Sol.**

38. In the reaction



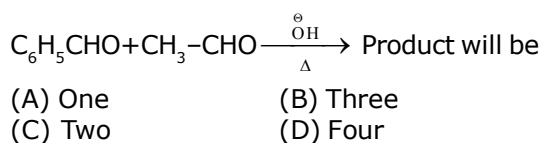
(X) and (Y) will respectively be:

- (A)  $\text{CH}_3-\text{CH}_2-\text{CHO}$  and  $\text{CH}_3-\text{CH}_2-\text{CHO}$   
(B)  $\text{CH}_3-\text{CHO}$  and  $\text{CH}_3-\text{CH}_2-\text{CHO}$   
(C)  $\text{CH}_3-\text{CHO}$  and  $\text{CH}_3-\text{CHO}$

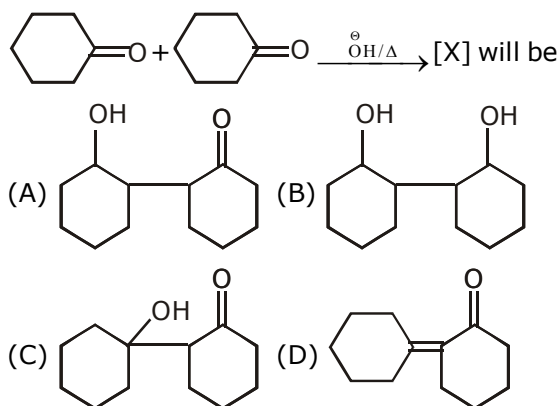


**Sol.**

39. Total number of products in the given reaction : (excluding stereoisomers)



40. In the reaction:



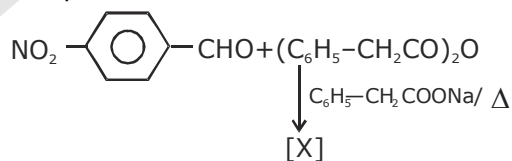
**Sol.**

41. Product of Perkin reaction is :

- (A)  $\alpha, \beta$ -unsaturated aldehyde  
(B)  $\beta$ -cyclohexyl  $\alpha, \beta$ -unsaturated aldehyde  
(C)  $\beta$ -Aryl- $\alpha, \beta$ -unsaturated acid  
(D) All of these

**Sol.**

42. The product of the reaction:



[X] will be:

- (A)  $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{COOH}$   
(B)  $\text{NO}_2-\text{C}_6\text{H}_4-\text{CH}=\text{CH}-\text{COOH}$   
(C)  $\text{C}_6\text{H}_5-\text{CH}=\text{C}(\text{C}_6\text{H}_4\text{NO}_2)-\text{COOH}$   
(D)  $\text{NO}_2-\text{C}_6\text{H}_4-\text{CH}=\text{C}(\text{C}_6\text{H}_5)-\text{COOH}$

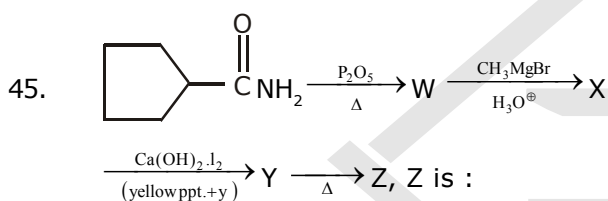
Sol.

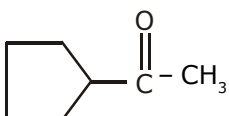
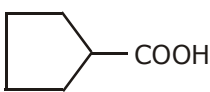
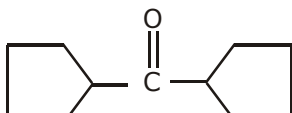

43. Cross cannizzaro reaction is example of  
 (A) Redox reaction  
 (B) Disproportionation  
 (C) Both (A) and (B)  
 (D) Only oxidation

Sol.

44. Which will give silver mirror test with Tollens reagent:  
 (A)  $C_6H_5CHO$  (B)  $CH_3-CHO$   
 (C)  $HCOOH$  (D) All of these

Sol.



- (A)   
 (B)   
 (C)   
 (D) 

Sol.

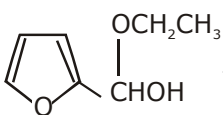
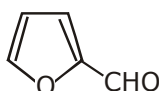
46. Cyanohydrin of which compound on hydrolysis will give lactic acid?

- (A)  $C_6H_5CHO$  (B)  $HCHO$   
 (C)  $CH_3CHO$  (D)  $CH_3-CH_2-CHO$

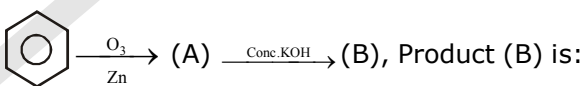
Sol.

47. Acetaldehyde cannot give:  
 (A) Iodoform test (B) Lucas test  
 (C) Benedict test (D) Tollens test

Sol.

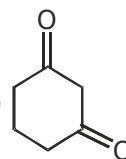
48. Compound  formed by the reaction of furfural  with ethanol is  
 (A) an aldol (B) an acetal  
 (C) a ketal (D) a hemiacetal

Sol.

49.   
 (A)  $\begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix}$  (B)  $\begin{matrix} CO_2H \\ | \\ CO_2H \end{matrix}$   
 (C)  $\begin{matrix} CH_2-OH \\ | \\ CO_2^- \end{matrix}$  (D)  $\begin{matrix} CO_2^- \\ | \\ CO_2^- \end{matrix}$

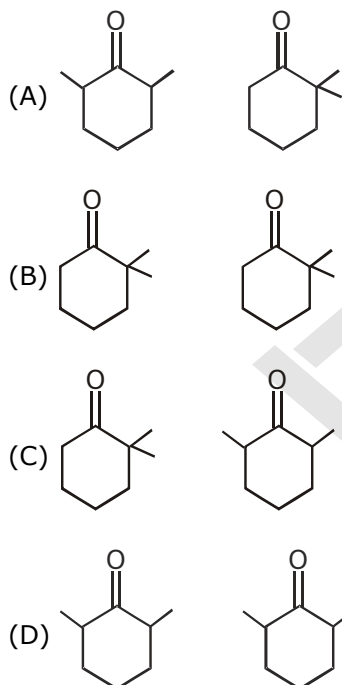
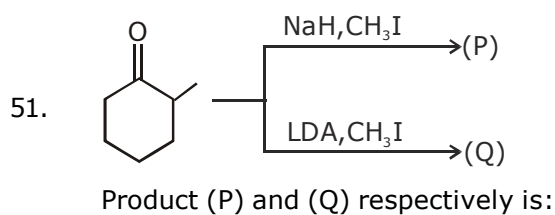
Sol.

50. Which of the following will react with  $NaOI$ ?

- (A)  $CH_3-C(=O)-H$  (B) 

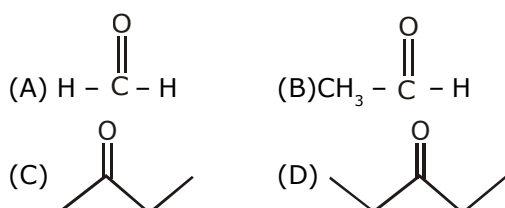


**Sol.**

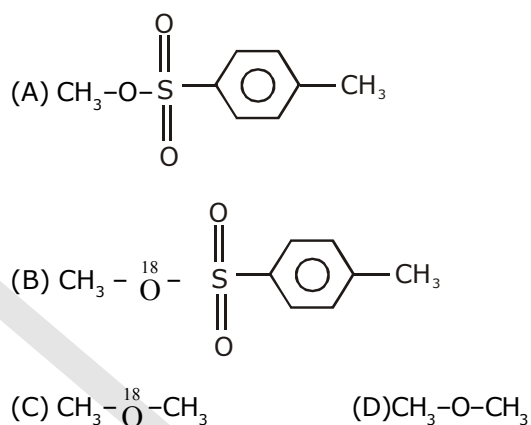
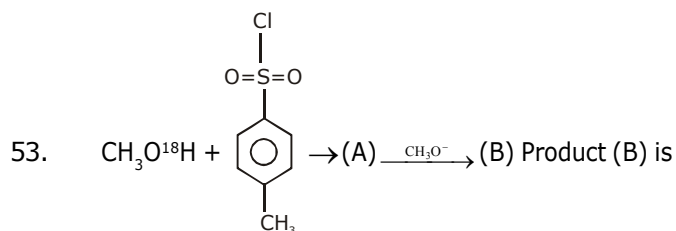


**Sol.**

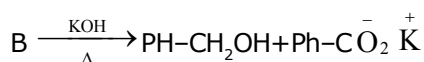
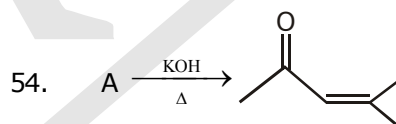
52. Which of the following compound not reacts with  $\text{NaHSO}_3$ ?



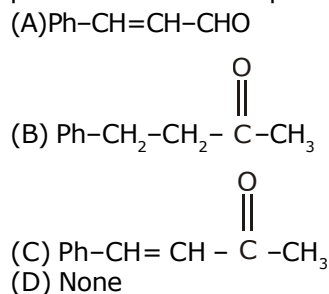
**Sol.**



**Sol.**



When A reacts with B in presence of  $\text{KOH}/\Delta$  product C is formed product C is ?

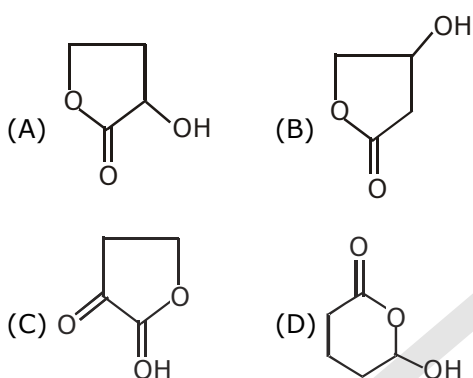


**Sol.**

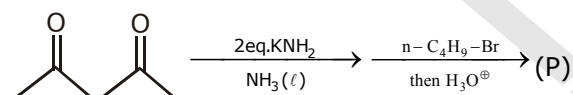
55.  $\text{Ph}-\text{CH}=\text{O} + \text{NH}_2-\text{NH}_2 \xrightarrow{\text{H}^+}$  (A). Product (A) is known as:  
 (A) Aldo-Oxime (B) Hydrazone  
 (C) Hydrate (D) Phenyl hydrazone

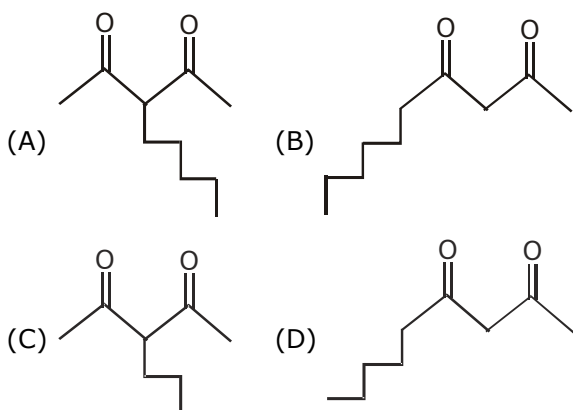
Sol.

56.  $\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}=\text{O} \xrightarrow[\text{(4) } \Delta]{\text{(1) KCN, (2) H}^+, \text{(3) H}_3\text{O}^+}$  (A), Product (A) is:

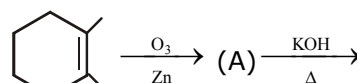


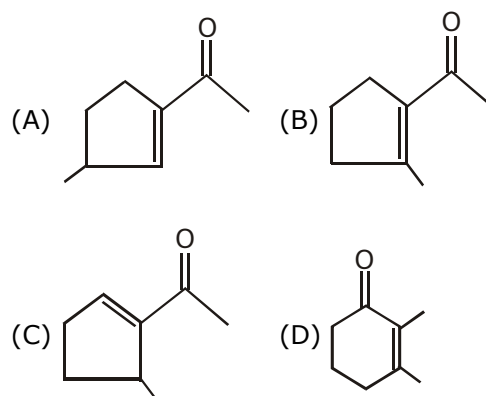
Sol.

57.  (P)  
 End product (P) of above reaction is:



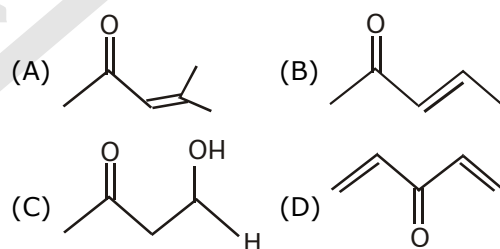
Sol.

58.   
 (B) Major product (B) is:



Sol.

59.  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3 + \text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \xrightarrow{\text{KOH}}$   
 (A) major. Product (A) is :



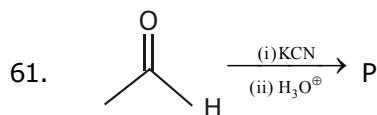
Sol.

60.  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} \xrightarrow[\Delta]{\text{CaO}}$  (A)  $\xrightarrow[\Delta]{\text{KOH}}$   
 (B)  $\xrightarrow[\text{(prolonged treatment)}]{\text{D}_2\text{O}/\text{DO}^\ominus}$  (C)

How many hydrogen is replaced by Deuterium

- (A) 2 (B) 10  
(C) 7 (D) 8

**Sol.**



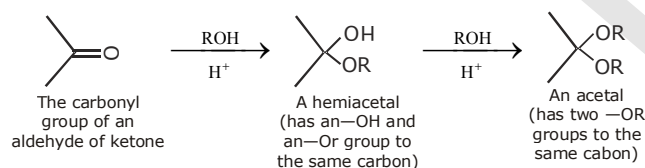
Find out the incorrect statement about the above given reaction

- (A) It is a nucleophilic addition reaction  
(B) Obtained product is present in racemic mixture  
(C) If the hydrolysis of obtained product give  $\alpha$ -hydroxy acid  
(D) It is a electrophilic addition reaction

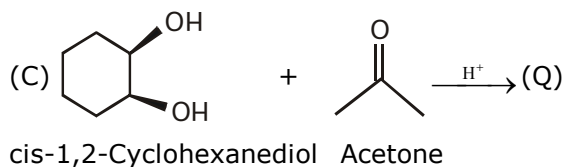
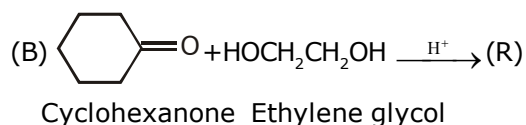
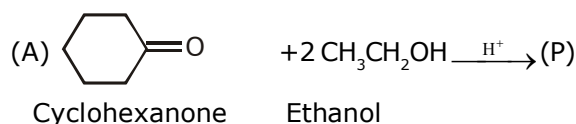
**Sol.**

**Comprehension : (Q.62 to Q.64):**

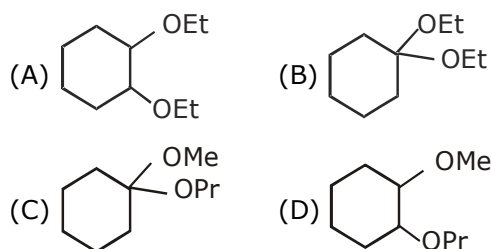
Aldehydes and ketones react with one molecule of an alcohol to form compounds called hemiacetals, in which there is one hydroxyl group and one ether-like group. Reaction of a hemiacetal with a second molecule of alcohol gives an acetal and a molecule of water. We study this reaction



Draw structural formulas for the hemiacetal and acetal formed from these reagents. The stoichiometry of each reaction is given in the problem.

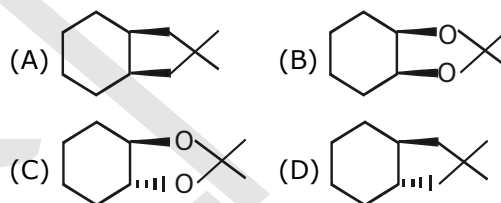


62. Product P is .



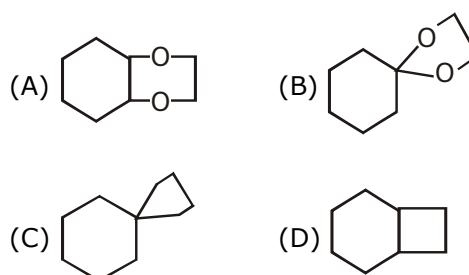
**Sol.**

63. Product Q is .



**Sol.**

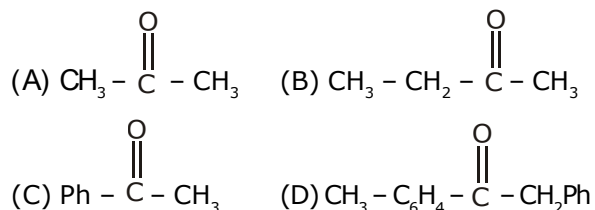
64. Product R is .



**Sol.**

**Exercise - II****(One or more than one option correct)**

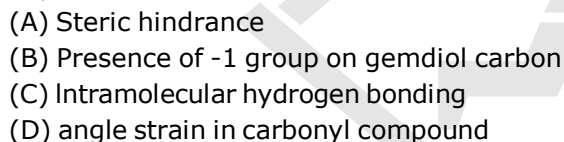
1. Which one of the following is mixed ketone (Aliphatic & aromatic):

**Sol.**

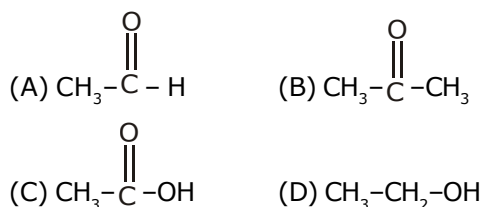
2. Two isomeric ketones, 3-pentanone and 2-pentanone can be distinguished by:

**Sol.**

3. Stability of hydrates of carbonyl compounds depends on:

**Sol.**

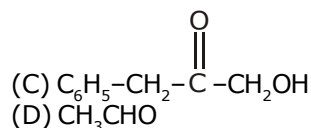
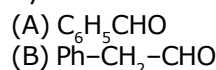
4. Which of following give positive test with 2,4-DNP?

**Sol.**

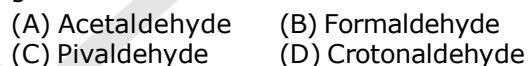
5. Fehling solution gives red precipitate with:  
 (A) Aromatic aldehyde (B) Aliphatic aldehyde  
 (C) Ketones (D)  $\alpha$ -hydroxy ketones

**Sol.**

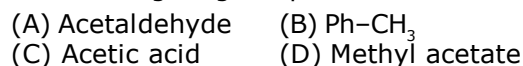
6. Silver mirror test with Tollens reagent is given by :

**Sol.**

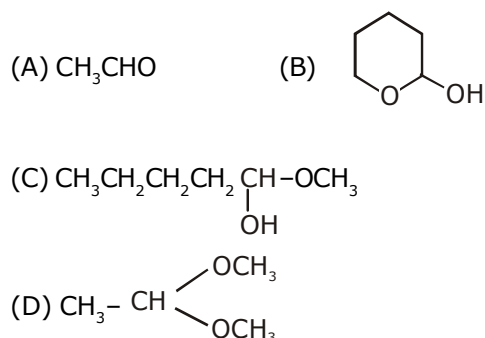
7. Which one of the following compounds will not give aldol:

**Sol.**

8. Schiff's reagent gives pink colour with:

**Sol.**

9. Which of the following compound will give positive Tollens test



Sol.

10. Mixture of  $\text{Ph}-\text{CHO}$  &  $\text{HCHO}$  is treated with  $\text{NaOH}$  then Cannizzaro reaction involves:
- (A) Oxidation of  $\text{HCHO}$   
 (B) Reduction of  $\text{HCHO}$   
 (C) Oxidation of  $\text{Ph}-\text{CHO}$   
 (D) Reduction of  $\text{Ph}-\text{CHO}$

Sol.

11.  $\text{PhCHO} + \text{HCHO} \xrightarrow{\text{Conc.KOH}}$
- Correct statement regarding reaction will be
- (A) It is an example of redox reaction  
 (B)  $\text{HCHO}$  is oxidised  
 (C) It is cross cannizzato reaction  
 (D)  $\text{Ph}-\text{CHO}$  is reduced

Sol.

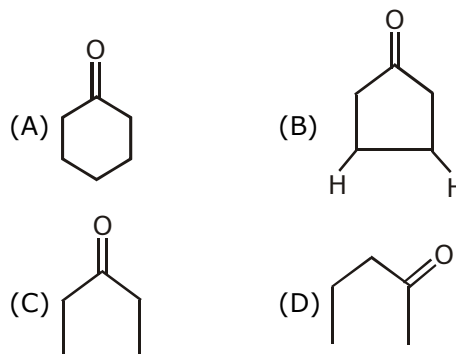
**Paragraph for Question Nos.12 to 14**

Carbonyl group show characteristic reaction of nucleophilic addition in which nucleophile attack in rate determining step on carbonyl carbon.

12. Which Ph is suitable for oxime formation
- (A) 4-5 (B) 1-2  
 (C) 8-10 (D) 12-14

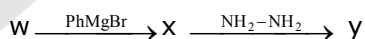
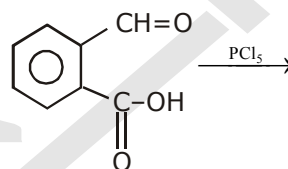
Sol.

13. Which of the reactant show geometrical isomerism when it react with hydrazine ( $\text{NH}_2-\text{NH}_2$ )

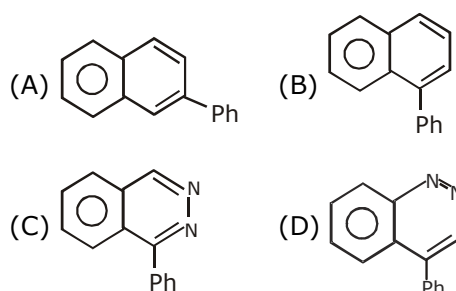


Sol.

- 14.



Identify final product 'y' of the above given reaction:



Sol.

15. Match list-I with list-II and select the correct answer using the codes give below the lists:

**List-I**

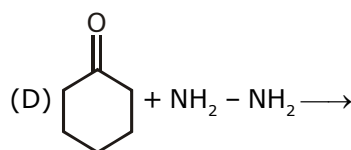
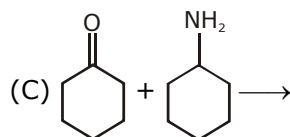
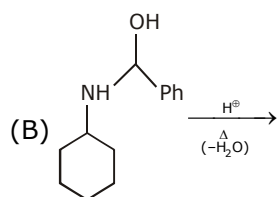
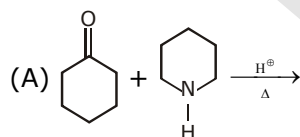
- (A)  $\text{CH}_2=\text{CH}-\text{CHO} \xrightarrow{\text{NaBH}_4}$
- (B)  $\text{C}_6\text{H}_5\text{CHO} + \text{Ph}-\text{NH}_2 \xrightarrow{\text{H}^+}$
- (C)  $\text{C}_6\text{H}_5\text{COCH}_3 + \text{CH}_3-\text{CH}_2-\text{NH}_2 \xrightarrow{\text{H}^+}$
- (D)  $\text{RCHO} + 2\text{RCH}_2\text{OH} \xrightarrow{\text{H}^+}$

**List-II**

- (P) Acetal  
(Q) Schiff's base  
(R) Unsaturated alcohol  
(S) Enamine

**Sol.**

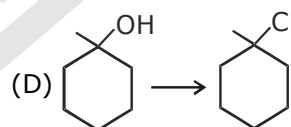
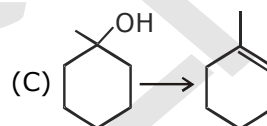
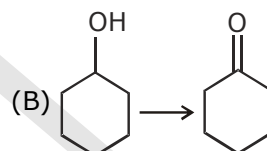
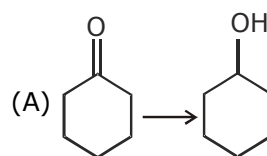
16. Match the following :

**Column I****Column II**

- (P) An enamine will form  
(Q) Schiff base will form  
(R) Hydrazone will form  
(S) Product form will undergo Lassaigne test

**Sol.**

17. **Column I**

**Column II****(Reagent used)**

- (P)  $\text{Al}(\text{OCHMe}_2)_3$  or  $\text{H}_2/\text{Ni}$   
(Q)  $\text{Al}(\text{OCMe}_2)_3$  or  $\text{CrO}_3$   
(R)  $\text{H}_3\text{PO}_4/\Delta$   
(S) conc. HCl

**Sol.**



## Exercise - III

## Subjective Level-I

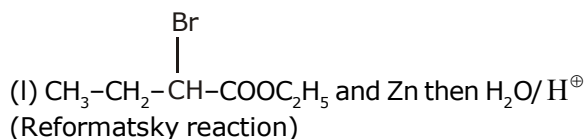
1. Predict the product of the reaction of propanal with each of the following

- Lithium aluminum hydride
- Sodium borohydride
- Hydrogen(nickel catalyst)
- Methylmagnesium iodide, followed by dilute acid.
- Sodium acetylide, followed by dilute acid
- Phenyllithium, followed by dilute acid
- Methanol containing dissolved hydrogen chloride
- Ethylene glycol, p-toluenesulfonic acid, benzene
- Aniline ( $C_6H_5NH_2$ )
- Dimethylamine, p-toluenesulfonic acid, benzene
- Hydroxylamine
- Hydrazine
- Product of part(I) heated in triethylene glycol with sodium hydroxide
- p- Nitrophenylhydrazine
- Semicarbazide
- Ethylidenetriphenylphosphorane [ $(C_6H_5)_3P^+-CHCH_3$ ]
- Sodium cyanide with addition of sulfuric acid
- Chromic acid

**Sol.**

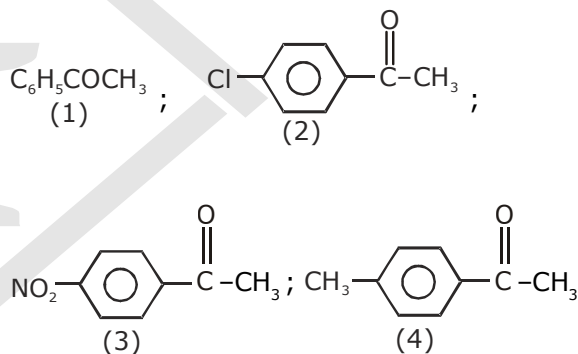
2. Give structure for the products of the reaction when butanal is treated with each of the following reagents

- $Ag(NH_3)_2^+ OH^-$  then  $HOH / H^+$
- $OH^- / HOH, \Delta$
- $NH_2OH / H^+$
- $C_6H_5Li$  then  $HOH$
- $C_6H_5CHO, OH^-, \Delta$
- $CH \equiv CNa$  then  $HOH / H^+$
- $CH_2OH-CH_2OH, H^+$
- $SH-CH_2-CH_2-CH_2-SH$  then Raney  $Ni/H_2$
- $CH_3MgBr$  then  $H_2O$
- $HCN$
- $NaBH_4$

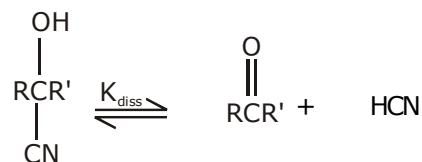


**Sol.**

3. (a) Arrange the following compounds in decreasing order of  $K_{eq}$  for hydrate formation.

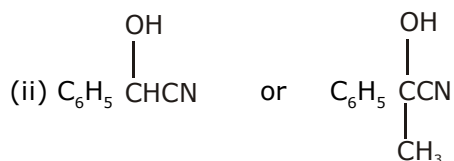
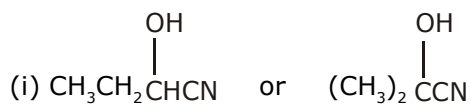


(b) Equilibrium constants for the dissociation ( $K_{diss}$ ) of cyanohydrins according to equation



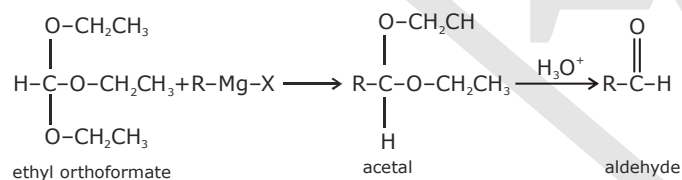
Cyanohydrin      Aldehyde    Hydrogen  
or ketone      cyanide

have been measured for a number of cyanohydrins. Which cyanohydrin in each of the following pairs has the greater dissociation constant?



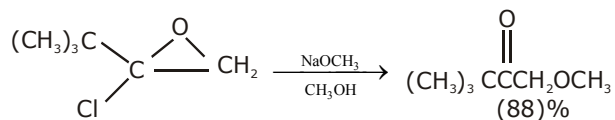
Sol.

4. Some grignard reagents react with ethyl orthoformate followed by acidic hydrolysis to give aldehydes. Propose mechanisms for the two steps in this synthesis.



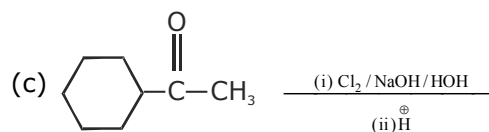
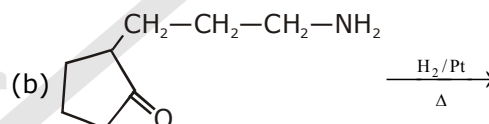
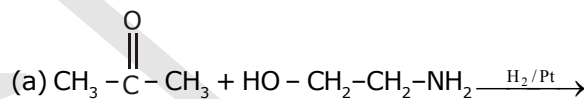
Sol.

5. Suggest a reasonable mechanism for each of the following reactions:



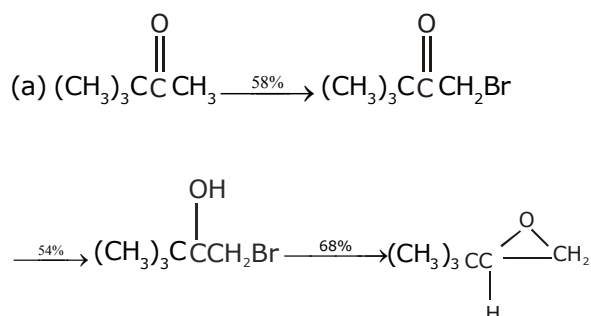
Sol.

6. Predict the organic products:



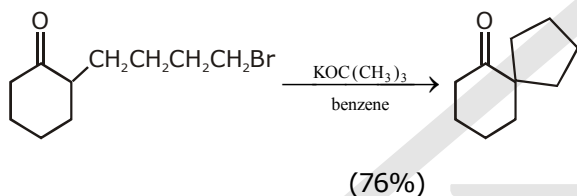
Sol.

7. A synthesis that begins with 3,3 - demethyl-2-butanone gives the epoxide shown. Suggest reagents appropriate for each step in the synthesis.



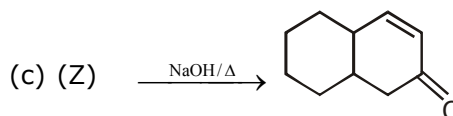
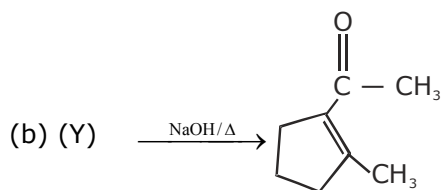
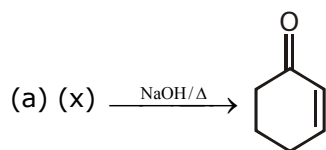
(b) Overall yield of the reaction is

8. Outline reasonable mechanisms for each of the following reactions:



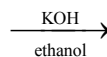
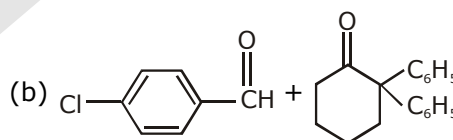
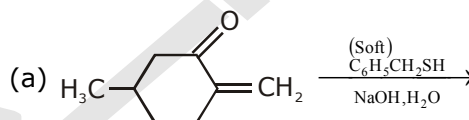
Sol.

9. Give the structure of the substance for each of the following reaction :



Sol.

10. Each of the following reactions has been reported in the chemical literature. Write the structure of the product(s) formed in each case.



Sol.

**EXERCISE – IV****PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

- Q.1** Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon ?

[AIEEE-2004]

- (A) Ethyl acetate (B) Acetic acid  
(C) Acetamide (D) Butan-2-one

Sol.

Sol.

- Q.2** Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid ?

[AIEEE-2004]

- (A) Phenol (B) Benzaldehyde  
(C) Butanal (D) Benzoic acid

Sol.

- Q.4** The increasing order of the rate of HCN addition to compounds A – D is -

[AIEEE 2006]

- (a) HCHO (b)  $\text{CH}_3\text{COCH}_3$   
(c)  $\text{PhCOCH}_3$  (d)  $\text{PhCOC}_6\text{H}_5$   
(A)  $d < b < c < a$  (B)  $d < c < b < a$   
(C)  $c < d < b < a$  (D)  $a < b < c < d$

Sol.

- Q.5** Which of the following on heating with aqueous KOH, produces acetaldehyde ?

[AIEEE 2009]

- (A)  $\text{CH}_3\text{COCl}$  (B)  $\text{CH}_3\text{CH}_2\text{Cl}$   
(C)  $\text{CH}_2\text{ClCH}_2\text{Cl}$  (D)  $\text{CH}_3\text{CHCl}_2$

Sol.

- Q.3** The best reagent to convert pent-3-en-2-ol into pent-3-in-2-one is -

[AIEEE-2005]

- (A) Acidic dichromate  
(B) Acidic permanganate  
(C) Pyridinium chloro-chromate  
(D) Chromic anhydride in glacial acetic acid

## LEVEL – II

## JEE ADVANCED

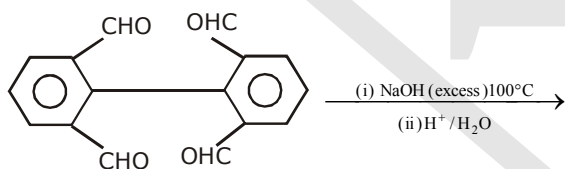
## Single Choice Question :

1. Compound A (molecular formula  $C_3H_8O$ ) is treated with acidified potassium dichromate to form a product B (molecular formula  $C_3H_6O$ ). B forms a shining silver mirror on warming with ammoniacal silver nitrate. B when treated with an aqueous solution of  $H_2NCONHNH_2$ , HCl and sodium acetate gives a product C. Identify the structure of C. [JEE 2002]

- (A)  $CH_3CH_2CH=NNHCONH_2$   
 (B)  $CH_3-C(=NNHCONH_2)-CH_3$   
 (C)  $CH_3-C(=NCONHNH_2)-CH_3$   
 (D)  $CH_3CH_2CH=NCONHNH_2$

Sol.

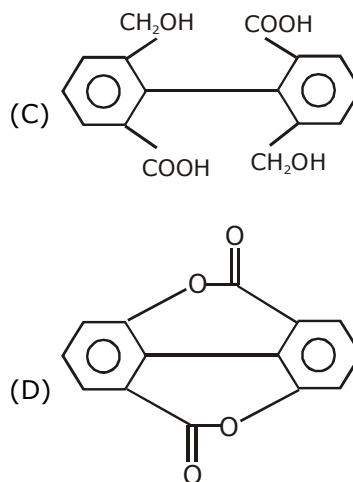
2.



any one of the products formed is:

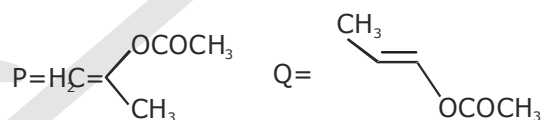
[JEE 2003]

- (A)
- (B)



Sol.

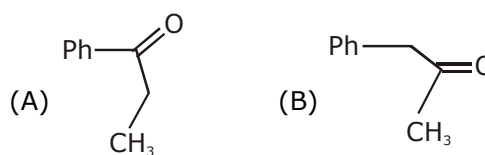
3. The products of acid hydrolysis of P and Q can be distinguished by [JEE 2003]

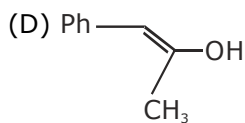
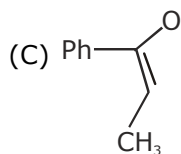


- (A) Lucas reagent (B) 2,4-DNP  
 (C) Fehling solution (D)  $NaHSO_3$

Sol.

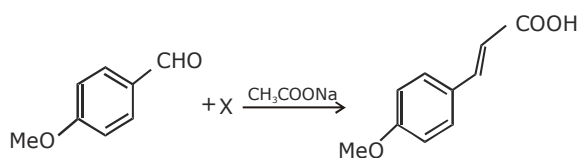
4.  $Ph-C \equiv C-CH_3 \xrightarrow{Hg^{2+} / H^+} A$  [JEE 2005]





Sol.

5.



What is X ?

[JEE 2005]

- (A)  $\text{CH}_3\text{COOH}$  (B)  $\text{BrCH}_2\text{COOH}$   
(C)  $(\text{CH}_3\text{CO})_2\text{O}$  (D)  $\text{CHO}-\text{COOH}$

Sol.

6. How will you convert butane-2-one to propanoic acid? [JEE 2005]

- (A) Tollen reagent (B) Fehling solution  
(C)  $\text{NaOH} / \text{I}_2 / \text{H}^+$  (D)  $\text{NaOH} / \text{NaI} / \text{H}^+$

Sol.

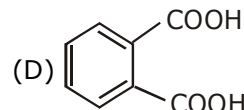
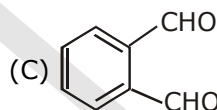
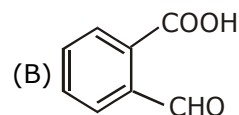
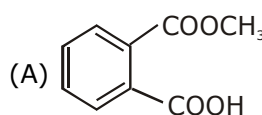
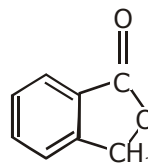
7. The smallest ketone and its next homologue are reacted with  $\text{NH}_2\text{OH}$  to form oxime. [JEE 2005]

- (A) Two different oximes are formed  
(B) Three different oximes are formed  
(C) Two oximes are optically active  
(D) All oximes are optically active

Sol.

8. Which of the following reactants on reaction with conc.  $\text{NaOH}$  followed by acidification gives the following lactone as the only product?

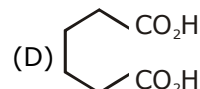
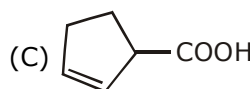
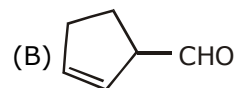
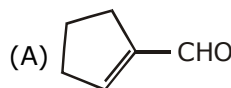
[JEE 2006]



Sol.

9. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound E. Compound E on further treatment with aqueous  $\text{KOH}$  yields compound F. Compound F is

[JEE 2007]



Sol.

10. Statement -1 : Glucose gives a reddish- brown precipitate with Fehling's solution. because  
Statement -2 : Reaction of glucose with fehling's solution gives CuO and gluconic acid.

[JEE 2007]

(A) Statement -1 is True ; Statement -2 is True; statement-2 is a correct explanation for statement -1

(B) Statement -1 is True; Statement -2 is True; statement-2 is NOT a correct explanation for statement -1

(C) Statement -1 is True, Statement -2 is False.

(D) Statement -1 is Fals, Statement -2 is True.

Sol.

MCQ:

11. Match the compounds/ion in column I with their properties / reaction in Cloumn II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS.

[JEE 2007]

**Column I**

- (A)  $C_6H_5CHO$   
(B)  $CH_3C \equiv CH$   
(C)  $CN^-$   
(D)  $I^-$

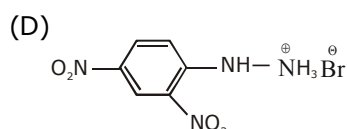
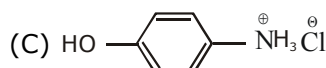
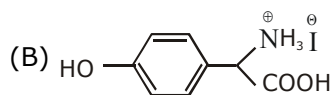
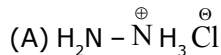
**Column II**

- (P) give precipitate with 2,4-dinitrophenylhydrazine  
(Q) gives precipitate with  $AgNO_3$   
(R) is a nucleophile  
(S) is involved in cyanohydrin formation

Sol.

12. Match the compound in Column I with their characteristic test (s)/reaction(s) given in Column II. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS

[JEE 2008]

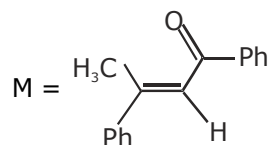
**Column I****Column II**

- (P) sodium fusion extract of the compound gives Prussian blue colour with  $FeSO_4$   
(Q) gives positive  $FeCl_3$  test  
(R) gives white precipitate with  $AgNO_3$   
(S) reacts with aldehydes to form the corresponding hydrazone derivative

Sol.

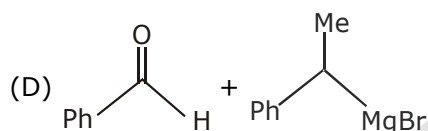
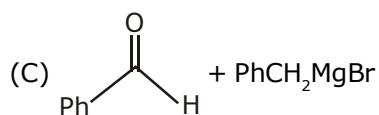
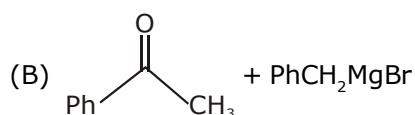
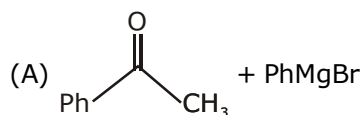
**Paragraph for Question No. 13 to 15**

A tertiary alcohol **H** upon acid catalysed dehydration gives a product **I**. Ozonolysis of **I** leads to compounds **J** and **K** compound **J** upon reaction with KOH gives benzyl alcohol and a compound **L**, whereas **K** on reaction with KOH gives only **M**. [JEE 2008]



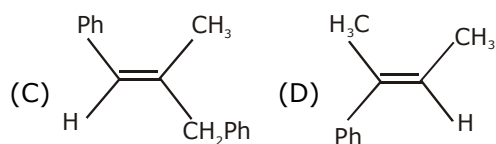
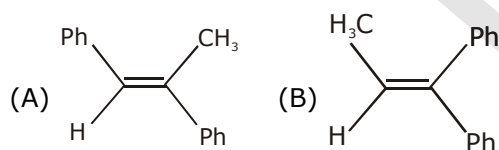
Sol.

13. Compound H is formed by the reaction of



Sol.

14. The structure of compound I is



Sol.

15. The structures of compounds J, K and L, respectively are

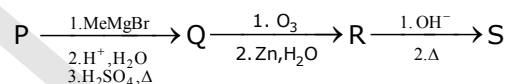
- (A) PhCOCH<sub>3</sub>, PhCH<sub>2</sub>COCH<sub>3</sub> and PhCH<sub>2</sub>COO<sup>-</sup>K<sup>+</sup>  
 (B) PhCHO, PhCH<sub>2</sub>CHO and PhCOO<sup>-</sup>K<sup>+</sup>  
 (C) PhCOCH<sub>3</sub>, PhCH<sub>2</sub>CHO and CH<sub>3</sub>COO<sup>-</sup>K<sup>+</sup>  
 (D) PhCHO, PhCOCH<sub>3</sub> and PhCOO<sup>-</sup>K<sup>+</sup>

Sol.

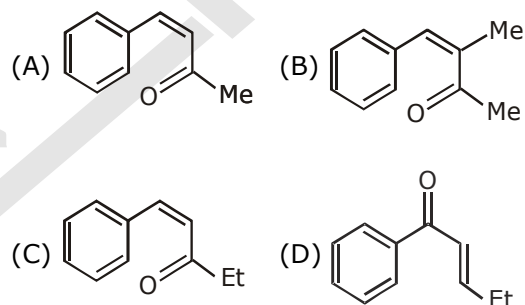
### Paragraph for Question Nos. 16 to 18

A carbonyl compound P, which gives positive iodoform test, undergoes reaction with MeMgBr followed by dehydration to give an olefin Q. Ozonolysis of Q leads to a dicarbonyl compound R which undergoes intramolecular aldol reaction to give predominantly S.

[JEE 2009]



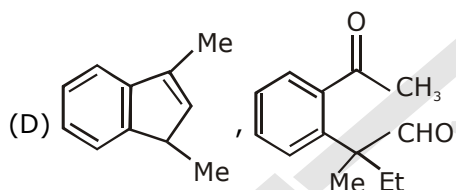
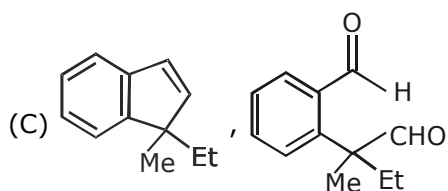
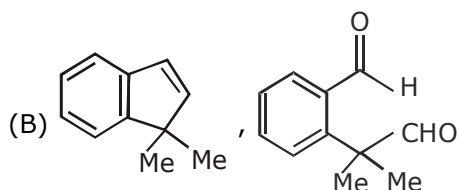
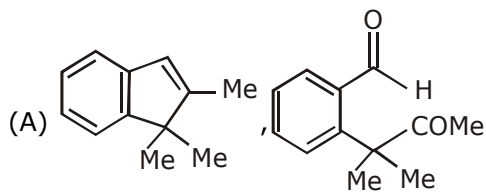
16. The structure of the carbonyl compound P is



Sol.

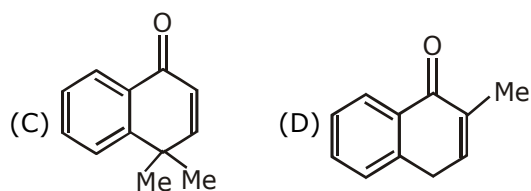
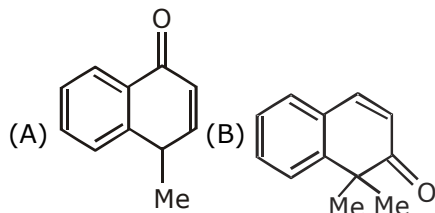
17. The structures of the products Q and R, respectively are





Sol.

18. The structure of the product S is :

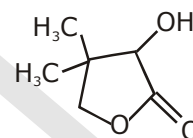


Sol.

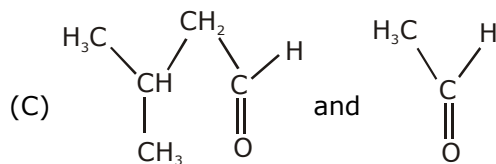
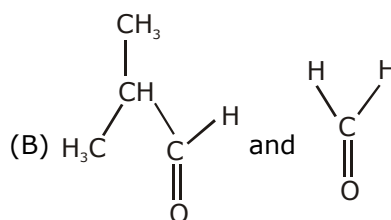
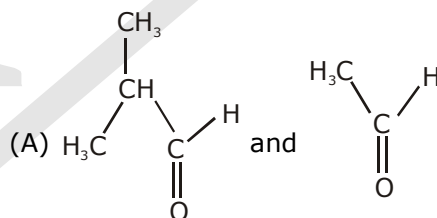
**Paragraph of Question Nos. 19 to 21**

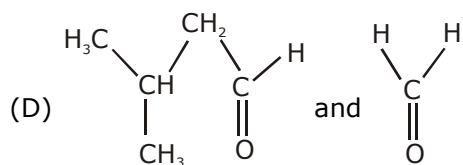
Two aliphatic aldehydes P and Q react in the presence of aqueous  $K_2CO_3$  to give compound R which upon treatment with HCN provides compound S. On acidification and heating, S gives the product shown below

[JEE 2010]

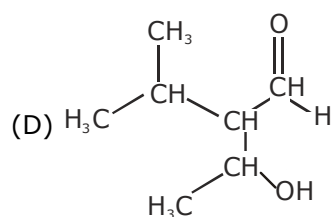


19. The compounds P and Q respectively are -



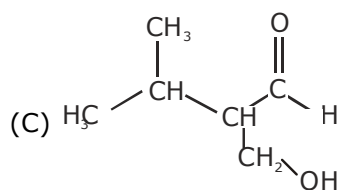
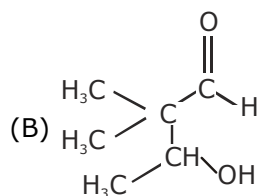
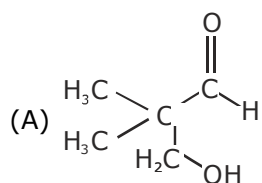


Sol.

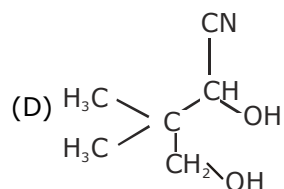
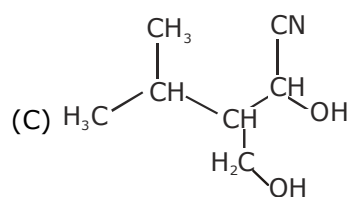
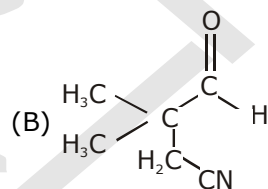
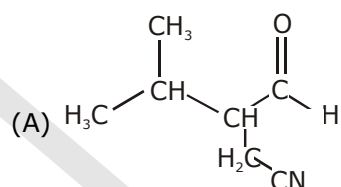


Sol.

20. The compound R is



21. The compound S is



Sol.

22. Five isomeric para -disubstituted aromatic compounds A to E with molecular formula  $C_8H_8O_2$  were given for identification. Based on the following observations, give structure of the compounds. **[JEE 2002]**

(i) Both A and B form a silver mirror with Tollen's reagent; also, B gives a positive test with  $FeCl_3$  solution  
 (ii) C gives positive iodoform test.  
 (iii) D is readily extracted in aqueous  $NaHCO_3$  solution.  
 (iv) E on acid hydrolysis gives 1, 4-dihydroxybenzene.

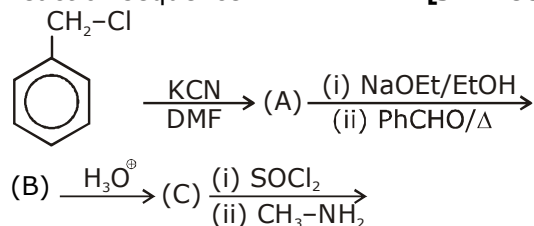
**Sol.**

23.  $C_6H_{12} \xrightarrow{HCl} C_6H_{13}Cl + (C)$   
 (A) (B)  
 $\xrightarrow[(-HCl)]{Alc.KOH} (D) \xrightarrow{\text{ozonolysis}} (E)$   
 (A)  $\xrightarrow{\text{ozonolysis}} (F) + (G) \xrightarrow{NaOH} HCOONa + 1^\circ \text{alcohol}$

(D) is isomer A. E gives negative test with Fehling solution but gives iodoform test F and G gives Tollen's test but do not give iodoform test. Identify A to G. **[JEE 2003]**

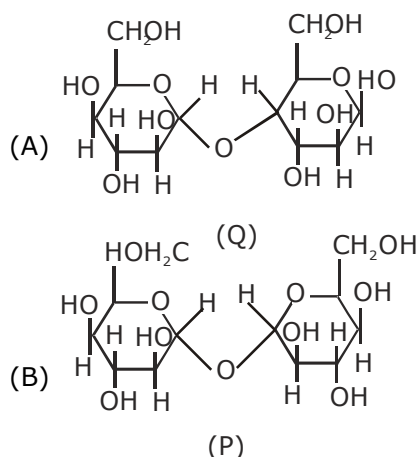
**Sol.**

24. Give major product A, B, C and D in following reaction sequence. **[JEE 2004]**

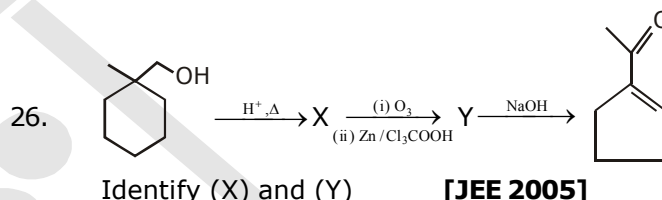


**Sol.**

25. Which of the following disaccharide will not reduce Tollen's reagent? **[JEE 2005]**

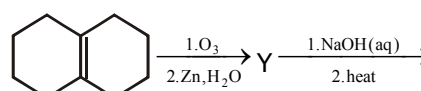


**Sol.**



**Sol.**

27. In the scheme given below the total number of intramolecular aldol condensation products formed from Y is **[JEE 2010]**



**Sol.**

# Answers


## Exercise-I

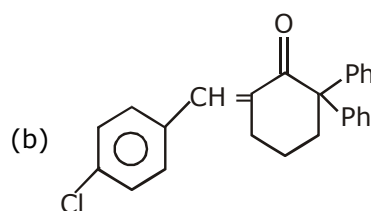
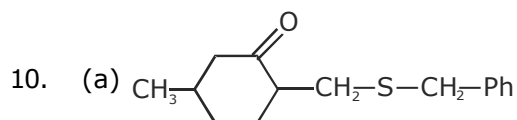
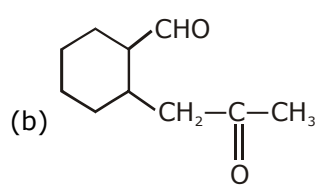
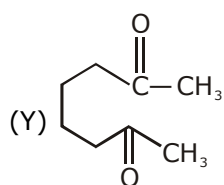
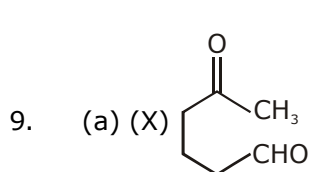
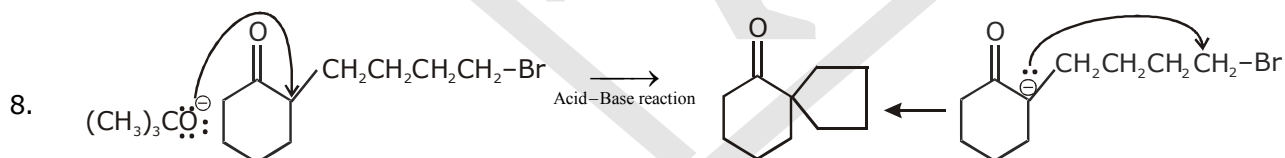
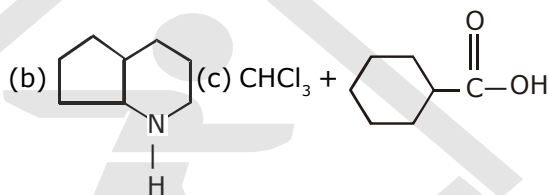
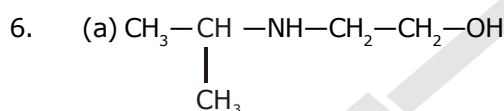
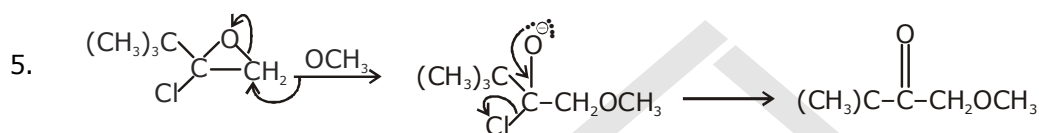
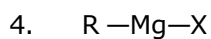
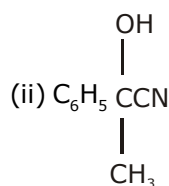
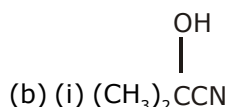
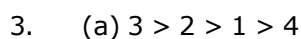
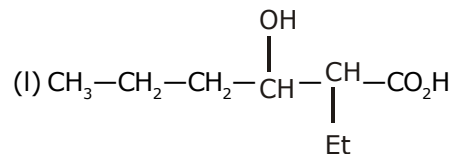
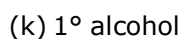
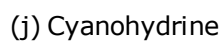
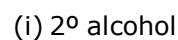
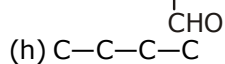
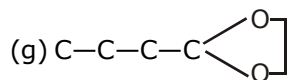
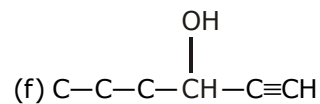
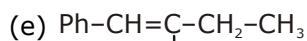
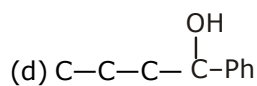
1. B	2. C	3. D	4. B	5. D	6. D	7. B
8. C	9. D	10. C	11. A	12. D	13. (i)C(ii)C	14. B
15. D	16. B	17. A	18. A	19. D	20. C	21. C
22. A	23. B	24. B	25. B	26. D	27. C	28. D
29. A	30. D	31. A	32. C	33. A	34. B	35. A
36. B	37. B	38. B	39. C	40. D	41. C	42. D
43. A	44. D	45. C	46. C	47. B	48. D	49. C
50. D	51. C	52. D	53. D	54. C	55. B	56. A
57. D	58. B	59. C	60. B	61. D	62. B	63. B
64. B						

## Exercise-II

1. C,D	2. AB	3. A,B,CD	4. A,B	5. B,D	6. A,B,C,D	7. B,C
8. A	9. A,B,C	10. A,D	11. A,B,C,D	12. A	13. D	14. C
15. A-R ; B-Q ; C-Q ; D-P			16. A→P,S ; B→Q, S ; C→Q, S ; D→R, S			
17. A→P ; B→Q ; C→R ; D→S						

## Exercise-III

1. (a)  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—OH}$  (b)  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—OH}$  (c)  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—OH}$
- (d)  $\text{CH}_3\text{—CH}_2\text{—CH(OH)—CH}_3$  (e)  $\text{CH}_3\text{—CH}_2\text{—CH(OH)—C}\equiv\text{CH}$  (f)  $\text{CH}_3\text{—CH}_2\text{—CH(OH)—Ph}$
- (g)  $\text{CH}_3\text{—CH}_2\text{—CH(OCH}_3\text{)—OCH}_3$  (h)  $\text{CH}_3\text{—CH}_2\text{—CH}$   (i)  $\text{CH}_3\text{—CH}_2\text{—CH=N—Ph}$
- (j)  $\text{CH}_3\text{—CH}_2\text{—CH(OH)—N(CH}_3\text{)—CH}_3$  (k)  $\text{C—C—C=N—OH}$  (l)  $\text{CH}_3\text{—CH}_2\text{—CH=N—NH}_2$
- (m)  $\text{CH}_3\text{—CH}_2\text{—CH}_3$  (p) P-Nitro phenyl hydrazone (o) semi carbazone
- (p)  $\text{CH}_3\text{—CH}_2\text{—CH=CH—CH}_3$  (q)  $\text{CH}_3\text{—CH}_2\text{—CH(OH)—CN}$  (r)  $\text{CH}_3\text{—CH}_2\text{—CO}_2\text{H}$
2. (a)  $\text{C—C—C—C(=O)—OH}$  (b)  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH=C(CH}_3\text{)—CH}_2\text{—CH}_3$  (c)  $\text{C—C—C—C—C=N—OH}$
- CHO

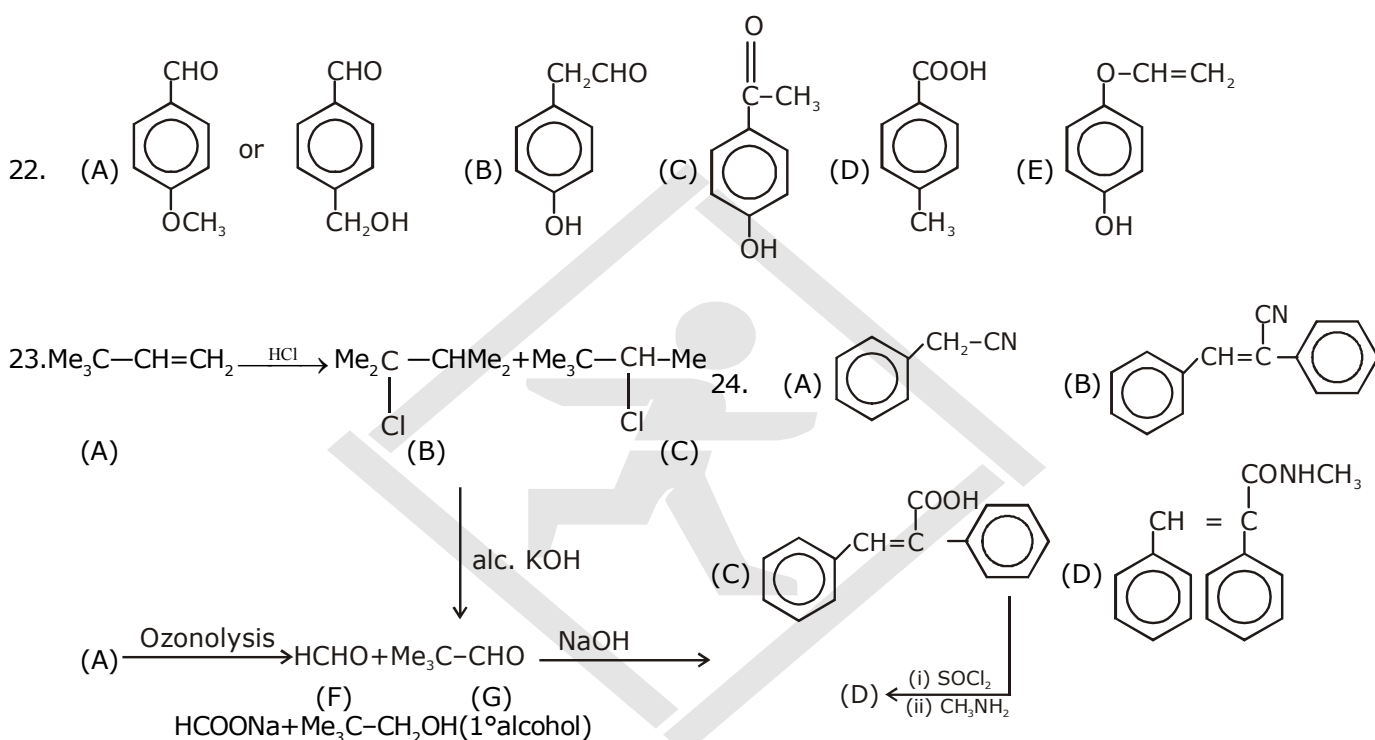


### Exercise-IV (LEVEL-1)

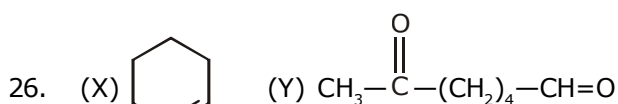
1. D    2. B    3. D    4. B    5. D

### Exercise-IV (LEVEL-2)

1. A    2. C    3. C    4. A    5. C    6. C  
 7. B    8. C    9. A    10. C  
 11. A → P, Q, S; B → Q, R; C → Q, R, S; D → Q, R  
 12. A → R, S; B → P, Q; C → P, Q, R; D → P, S    (OR) A → R; B → P, Q; C → P, Q, R; D → P  
 13. B    14. A    15. D    16. B    17. A    18. B    19. B  
 20. A    21. D



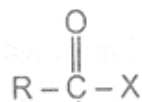
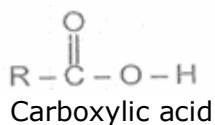
25. In structure (P) both the rings are present in acetyl form therefore it will not hydrolyse in solution that why Tollen's solution cannot react with this.  
 In structure (Q) one ring present in the form of hemiacetal. This will hydrolysed in solution it can reduce Tollen's solution.



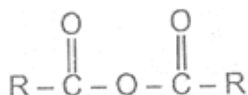
27. 1

## Carboxylic Acids & Acid Derivatives

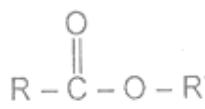
## Introduction :



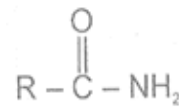
Acid halide



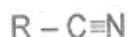
anhydride



ester

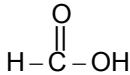
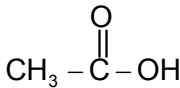
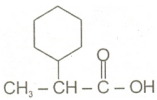
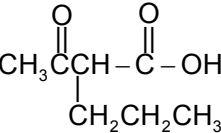
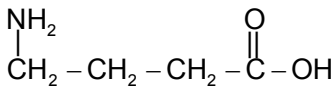
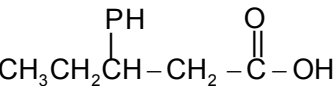
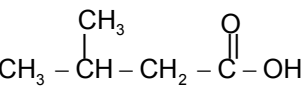
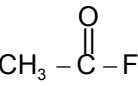
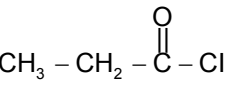
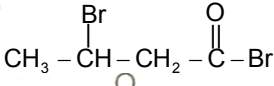
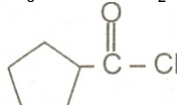


amide

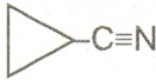
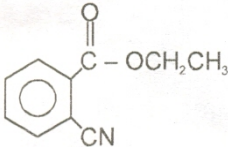
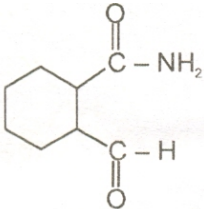


nitrile

**Table – 1 : IUPAC Nomenclature of Acid derivatives :-**

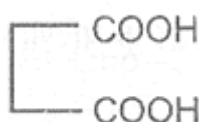
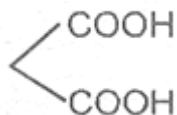
Compound	IUPAC Name
(1) 	Methanoic acid
(2) 	Ethanoic acid
(3) 	2- Cyclohexylpropanoic acid
(4) 	3- Oxo-2- propylbutanoic acid
(5) 	4- Aminobutanoic acid
(6) 	3- Phenylpentanoic acid
(7) 	3- Methylbutanoic acid
(8) 	Ethanoylchloride
(9) 	Propanoylchloride
(10)  	3- Bromobutanoylbromide

(11)	Cyclopentanecarbonyl chloride
(12)	Ethanoid anyhydride
(13)	Trifluoroethanoic anyhydride
(14)	1,2- Benzenedicarboxylic anyhydride

$\text{CH}_3 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{H}$	Ethanoic methanoic anyhydride
$\text{CH}_3\text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{CF}_3$	Trifluoroethanoic propanoic anyhydride
	Cyclopropane carbonitrile
$\text{CH}_3 - \text{CH}_2 - \overset{\text{CN}}{\underset{ }{\text{CH}}} - \text{CH}_2 - \text{COOH}$	3- Cyanopentanoci acid
	Ethyl o-cyanobenzoate
	2- Formylcyclohexane carboxamide
$\text{CH}_3 - \text{CH}_2 - \overset{\text{OH}}{\underset{ }{\text{CH}}} - \text{C} \equiv \text{N}$	2- Hydroxyutane nitrile

## Dicarboxylic acids

If the subsituent is a second carboxyl gropu, we have a dicarboxylic acid. For example :

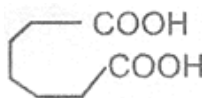
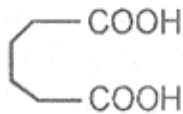
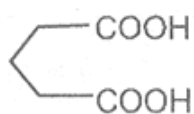




Oxalic acid  
Ethanedioic acid

Malonic acid -1, 3-  
dioic acid

Succinic acid -1, 4-  
dioic acid



Glutaric acid  
Pentane-1, 5-dioic acid

Adipic acid  
Hexane-1, 6-dioic acid

Pimelic acid  
Heptane-1, 7-dioic acid

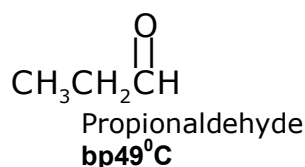
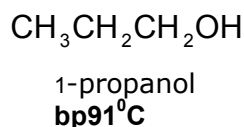
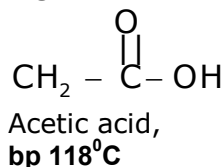
HOOCCH<sub>2</sub>COOH  
Malonic acid  
Propanedioic acid

HOOCCH<sub>2</sub>CH<sub>2</sub>COOH  
Succinic acid  
Butanedioic acid

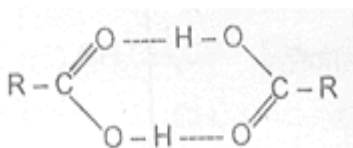
HOOCCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH  
Adipic acid  
Hexanedioic acid

## Physical properties of acids and acid derivatives :

(1) Boiling point :



The high boiling points of carboxylic acids is the result of formation of a stable hydrogen-bonded dimer.



Hydrogen bonded acid dimer

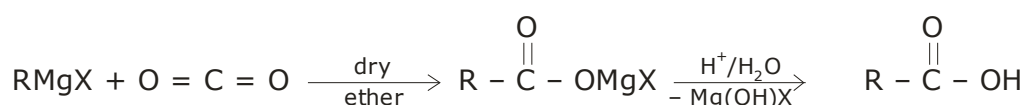
(2) Solubility :

Carboxylic acids form hydrogen bonds with water and the lower molecular weight carboxylic acids (upto 4 carbon atoms) are miscible with water.

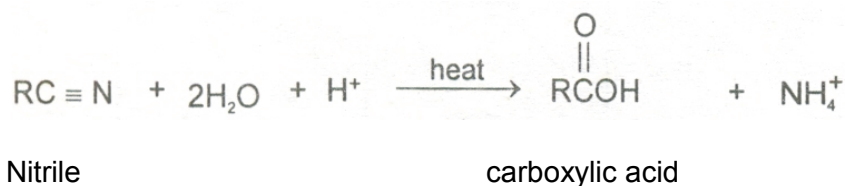
Acid derivatives (esters, acid chlorides, anhydride, nitriles and amides) are soluble organic solvents such as alcohols, ethers, chlorinated alkanes and aromatic hydrocarbons.

## Methods of preparation of carboxylic acids

1. Synthese of carboxylic acids by the carboxylation of grignard reagents



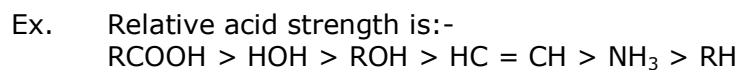
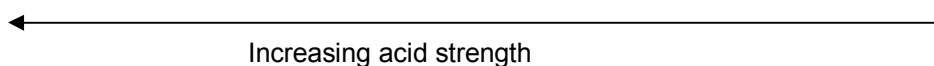
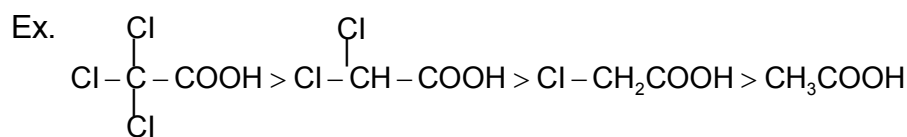
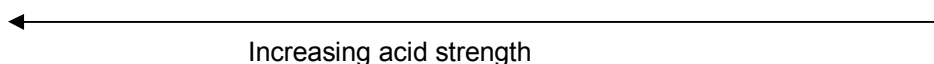
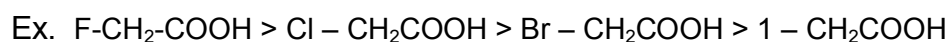
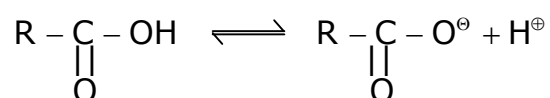
2. Synthesis of Carboxylic acids by the hydrolysis of nitriles Mechanism :



## Chemical Reactions

1. Acidic strength :

Acidity of carboxylic acids :-

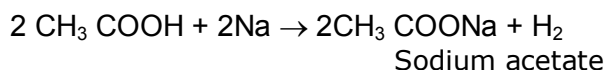


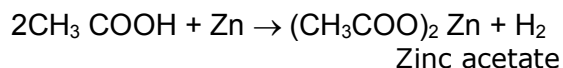
Note:- Acidity of acids is compared by comparing stability of conjugate base

2. **Reaction involving removal of proton from -OH group.**

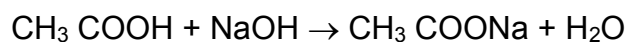
(1) Action with blue litmus : All carboxylic acids turn blue litmus red.

(2) Reaction with metals :

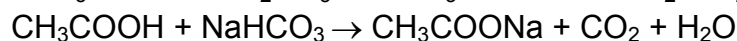
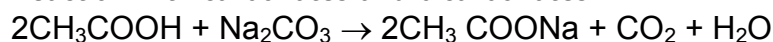




(3) Reaction with alkalies :

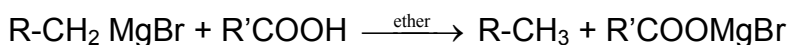


(4) Reaction with carbonates and bicarbonates :

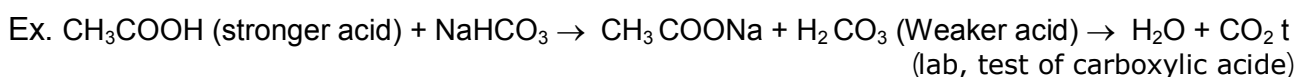
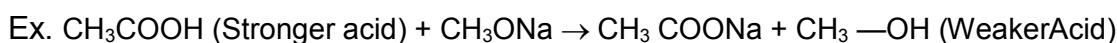


Reaction of carboxylic acid with aqueous sodium carbonate solution produces brisk effervescence. However most phenols do not produce effervescence. Therefore, the reaction may be used to distinguish between carboxylic acids and phenols.

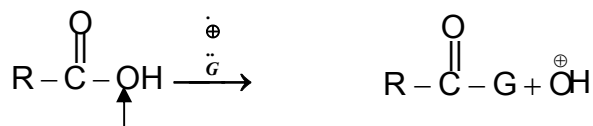
(5) Reaction with grignard reagent :



**Note** : A stronger acid displaces a weaker acid from salt of the weaker acid.



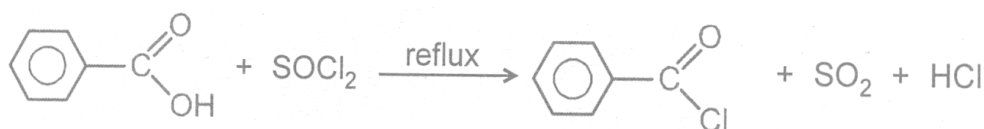
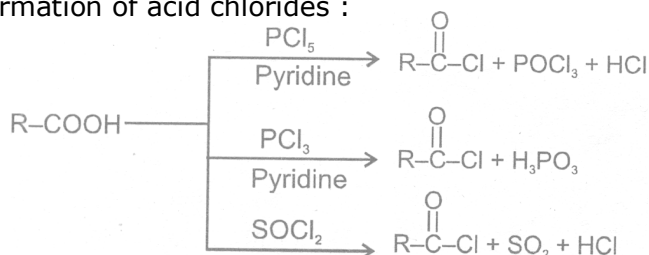
### 3. Reaction involving replacement of –OH group



Strong bases so not a                      basicity must be

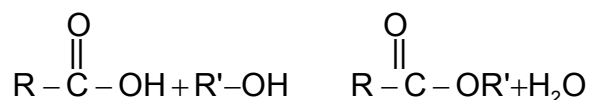
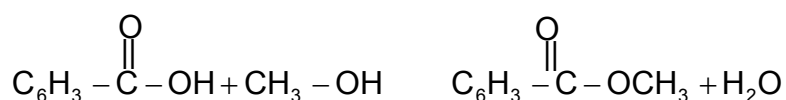
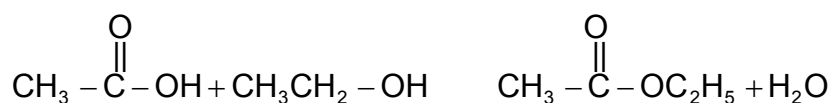
Good leaving group                      less than basicity of G–

(1) Formation of acid chlorides :

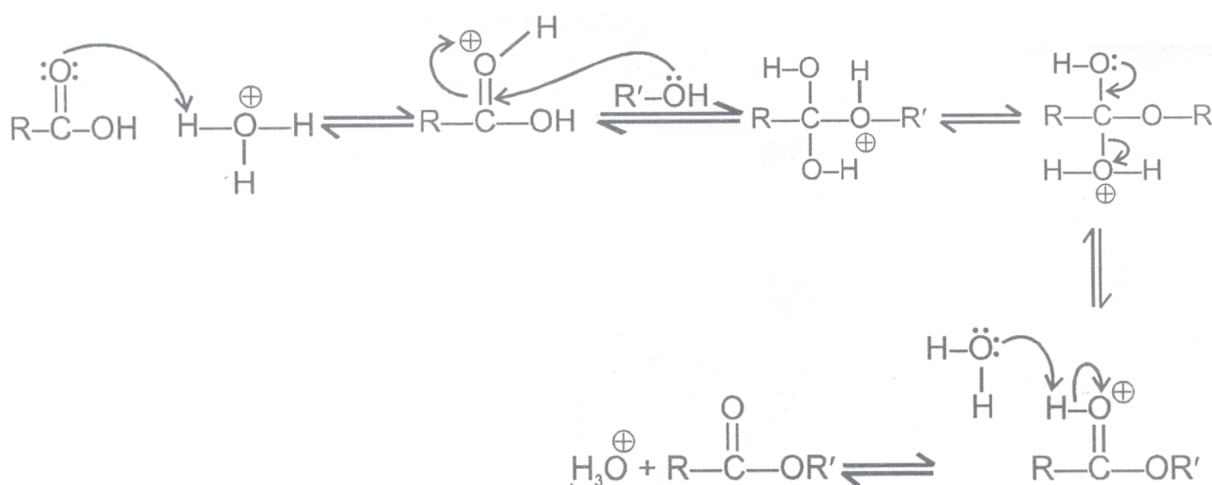


## (2) Fisher Esterification

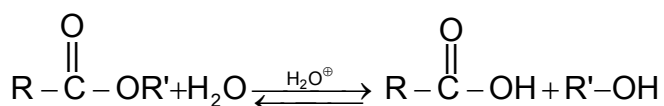
Carboxylic acid react with alcohol to form esters through a condensation reaction known as esterification.

**General Reaction :****Specific Example:**

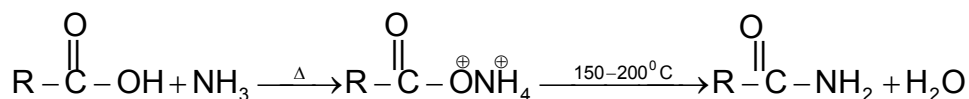
Mechanism : ( Acid catalysed esterification )



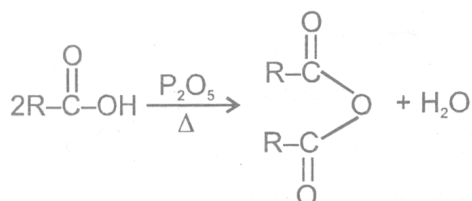
If we follow the forward in this mechanism, we have the mechanism for the acid catalysed esterification of an acid. If however, we follow the reverse reactions, we have the mechanism for the acid catalysed hydrolysis of an ester. Acid catalysed ester hydrolysis.



## (3) Formation of amides :



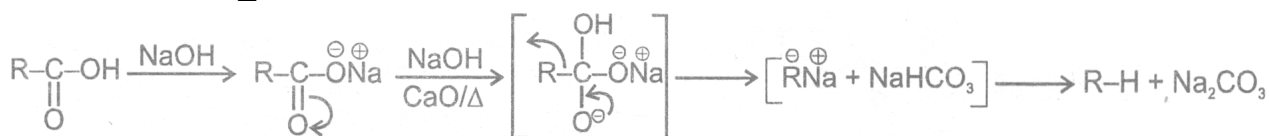
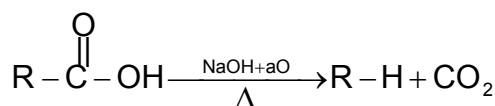
(4) Formation of acid anhydride :



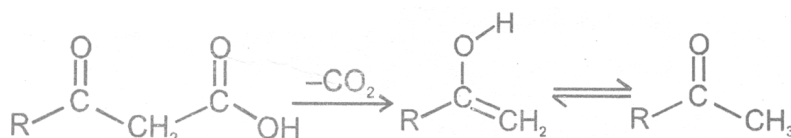
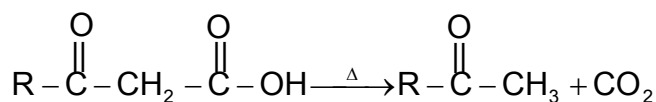
#### 4. Decarboxylation reactions:

(1) Soda-lime decarboxylation :

**General reaction:**

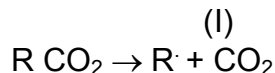
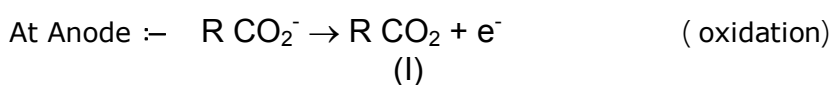
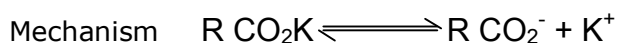
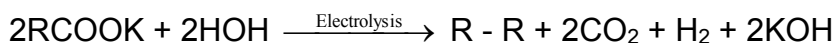


(2) Decarboxylation of  $\beta$ - keto carboxylic acids :

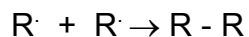


$\beta$  - keto acid

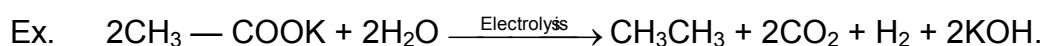
(3) **Kolbe electrolysis**



(II)



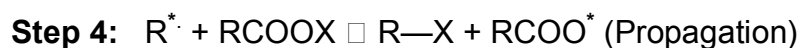
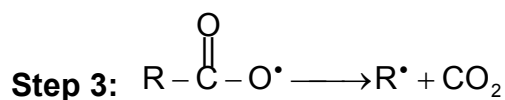
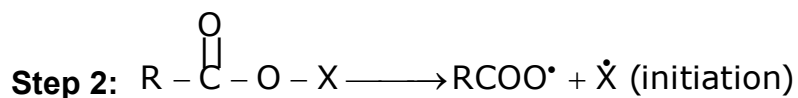
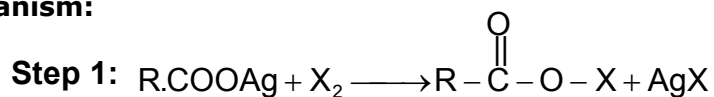
If n is the number of carbon atoms in the salt of carboxylic acid, the alkane formed has 2(n-1) carbon atoms.



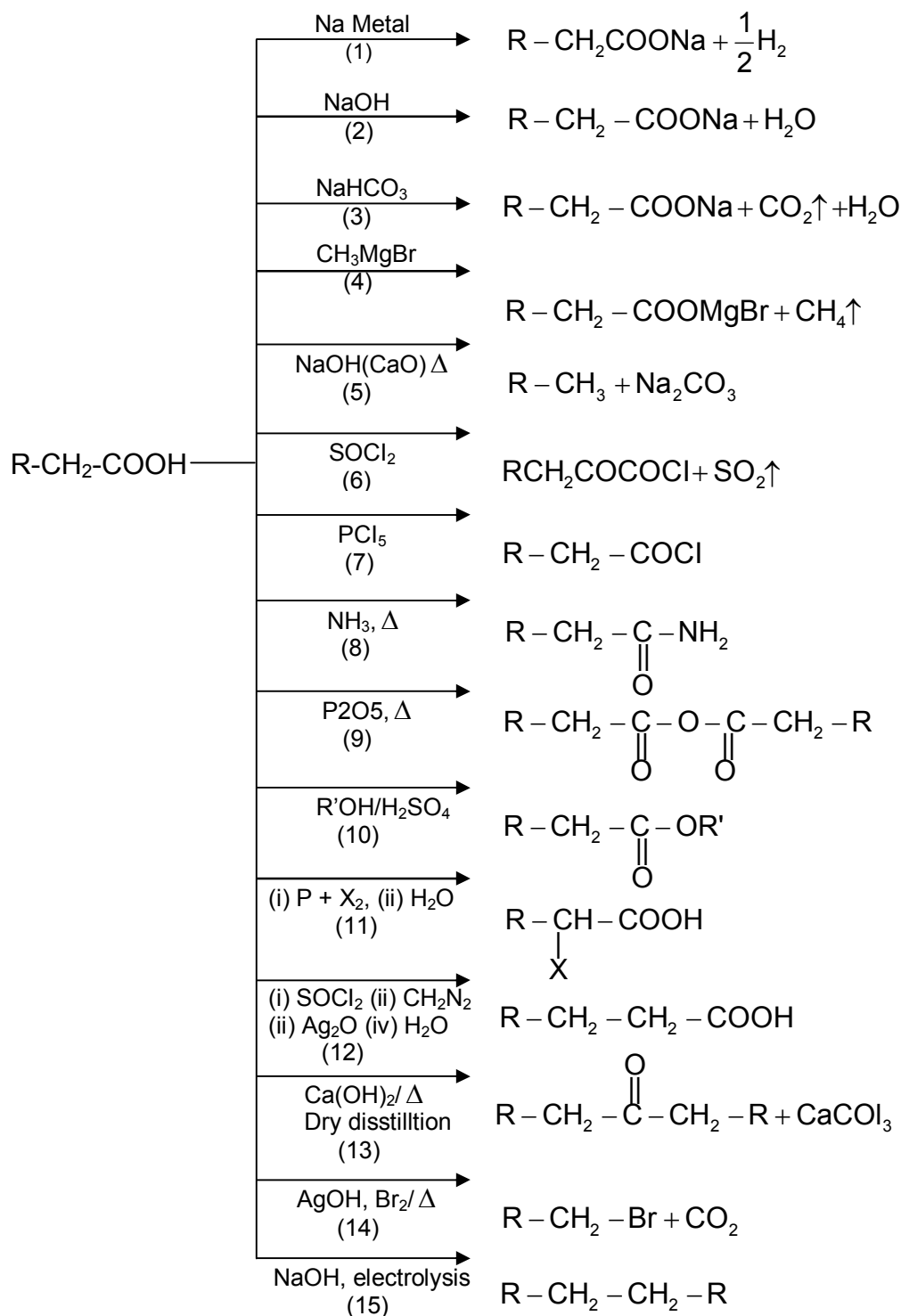
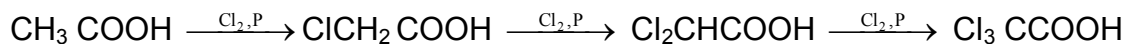
**(4) Hunsdiecker Reaction (Bromo-decarboxylation):**



**Mechanism:**

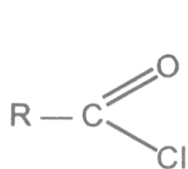


### 5. HVZ Reaction (Halogenation of aliphatic acids and Substituted acids)

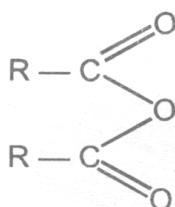


### Carboxylic Acid Derivatives

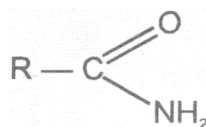
Closely related to the carboxylic acids and to each other are a number of chemical families known as functional derivatives of carboxylic acids : acid chloride, anhydrides, amide, and esters, These derivatives are compounds in which the -OH of a carboxyl group has been replaced by -Cl, -OOCR, -NR<sub>2</sub> or -OR



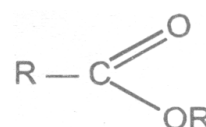
Acid chloride



Anhydride



Amide

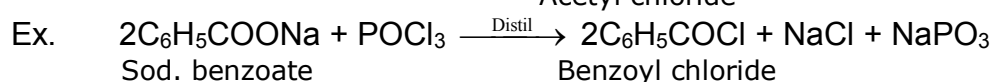
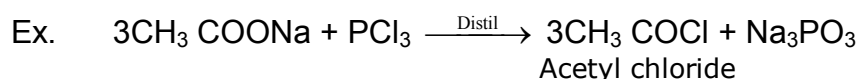
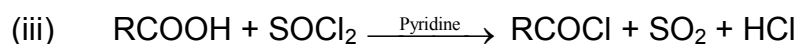
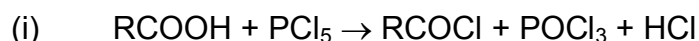


Ester

They all contain the acyl group ,  $\text{R}-\text{C} \begin{array}{l} \text{=O} \\ \text{---} \end{array}$

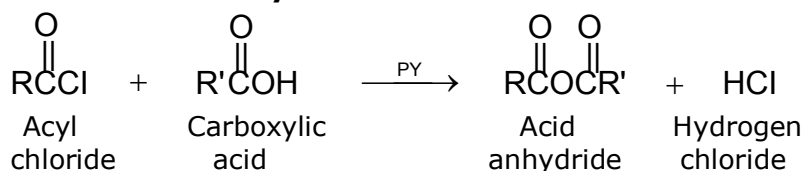
### (A) Acid halides

#### Methods of preparations of Acyl halides



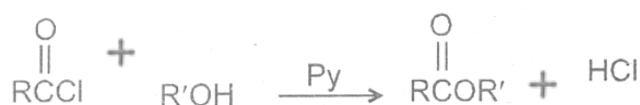
## Chemical Reactions

### (1) Reaction with carboxylic acids

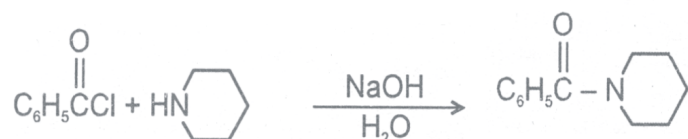
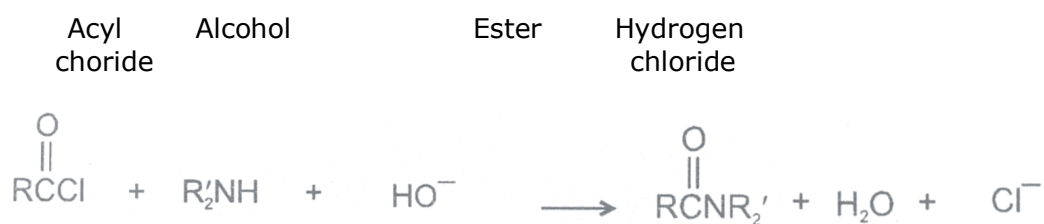


### (2) Reaction with alcohols

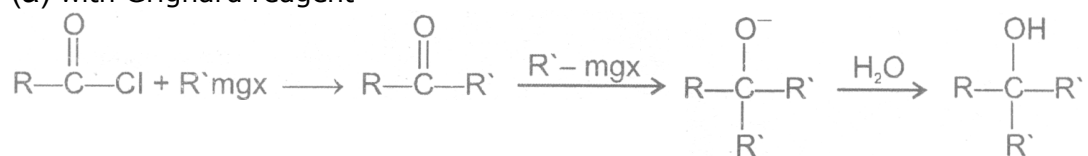
Acyl chlorides react with alcohols to form esters. The reaction is typically carried out in the presence of pyridine.





**(3) Hydrolysis****(4) Reaction of acid halide with organometallic**

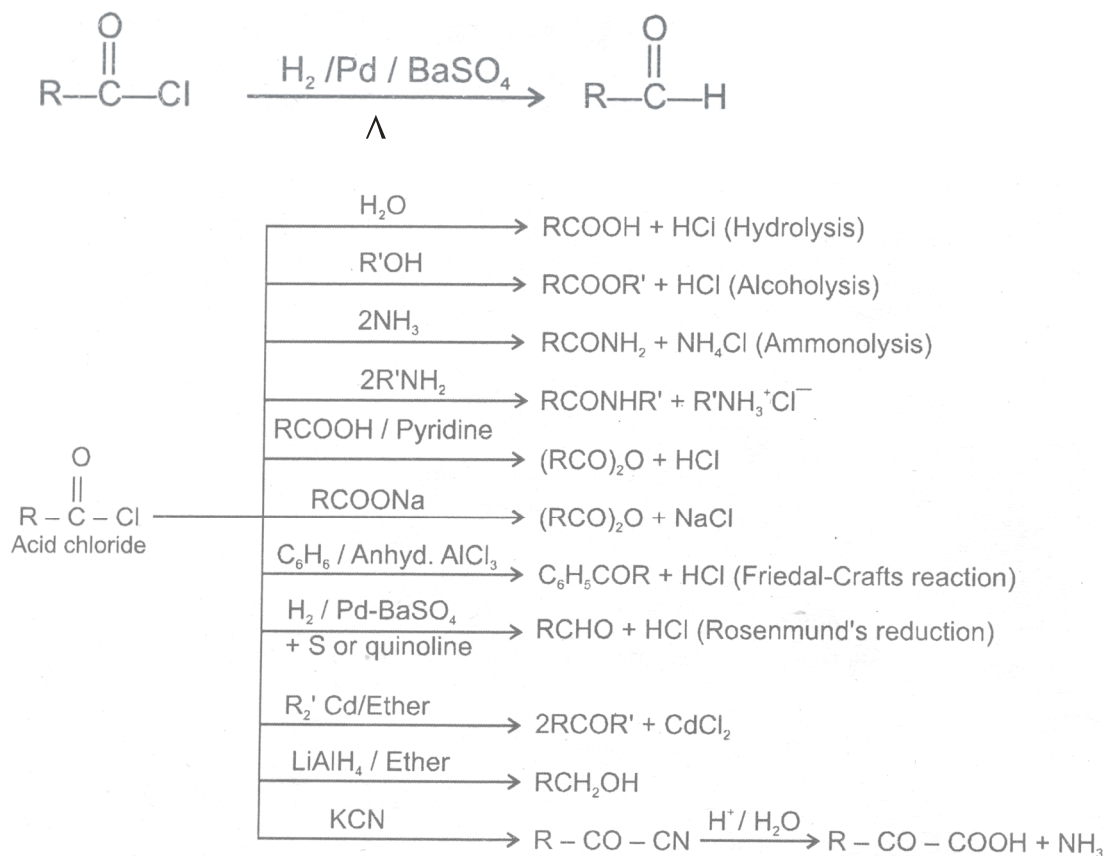
(a) with Grignard reagent



(b) Reaction with Gilman reagent

(a) Reduction  $\text{LiAlH}_4$ 

(b) Reduction with  $\text{H}_2/\text{Pd}/\text{BaSO}_4$  (Rosenmund reduction)



## (B) Acid amides

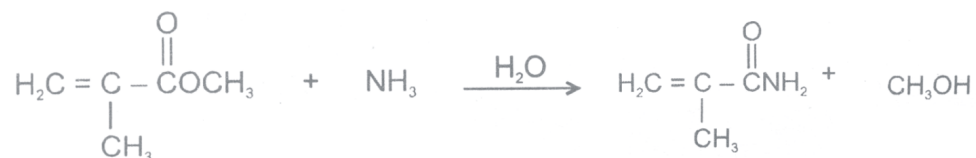
### Methods of preparation of acids amides

1. By reaction of esters with ammonia and amines

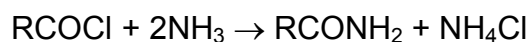


Ammonia is more nucleophilic than water, making it possible to carry out this reaction using aqueous ammonia<sup>†</sup>

Ex.



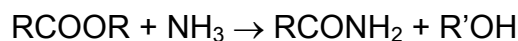
2. From acid halides



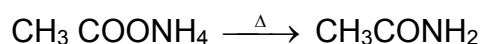
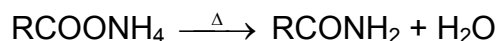
3. **From anhydride**



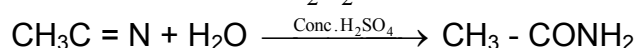
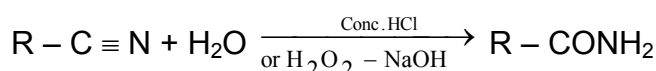
4. **From esters**



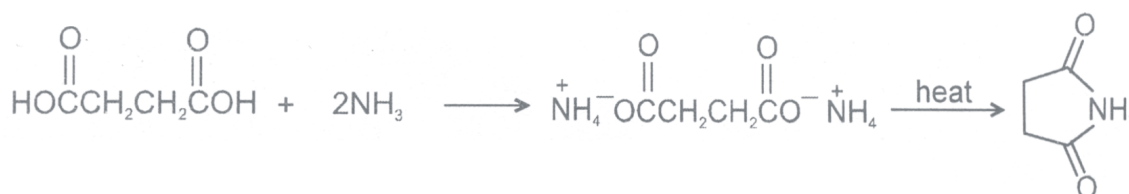
5. **From ammonium salt of carboxylic acid**



6. **From cyanides**



7.



**Chemical Reactions**

(1) **Hoffmann rearrangement**

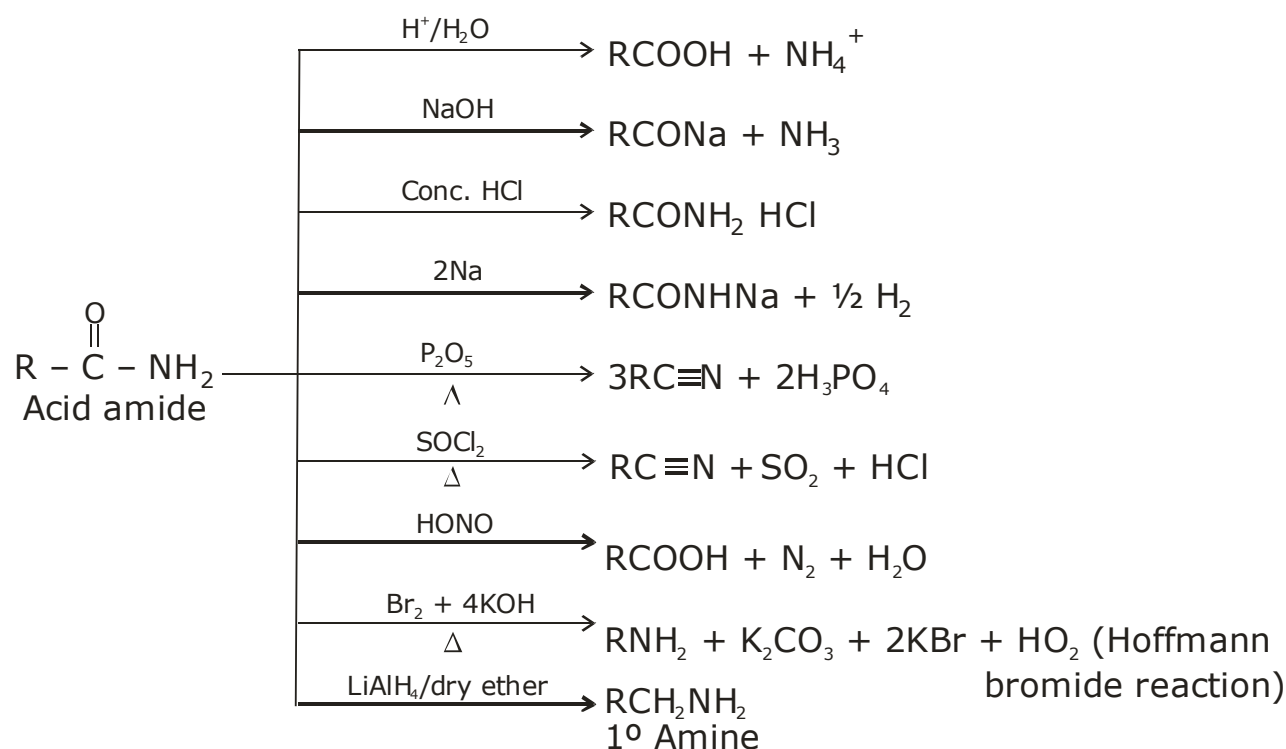
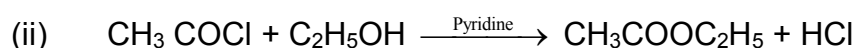
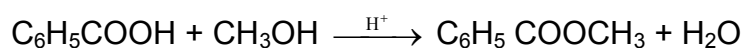
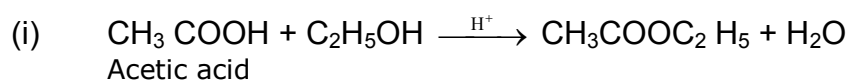
**General reaction**



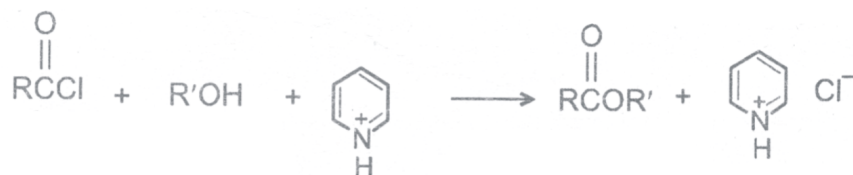
(2) **Hydrolysis of amides**



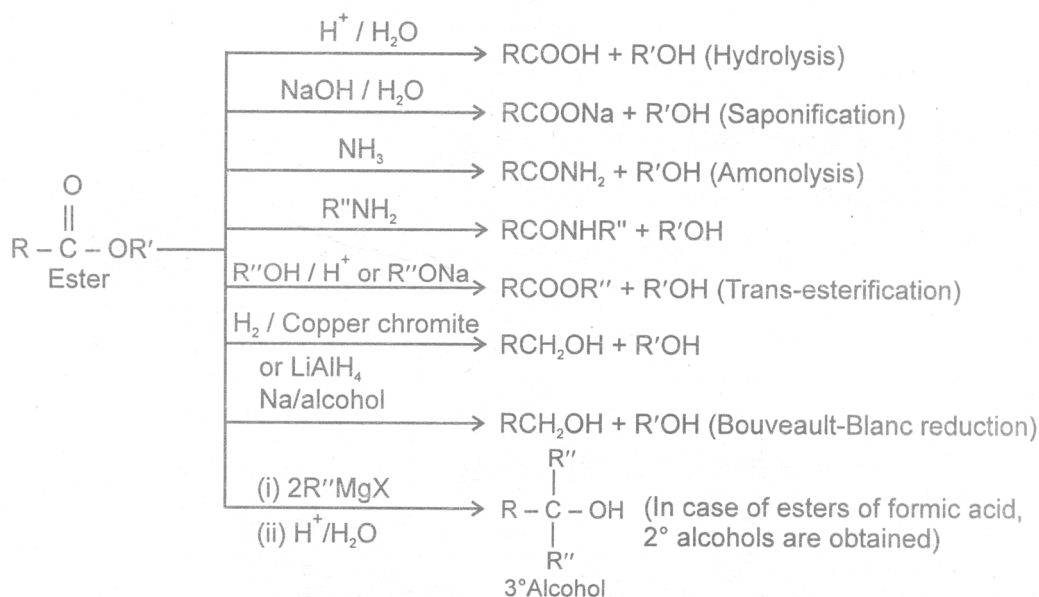
In acid, however, the amine is protonated, giving an ammonium ion,  $\text{R}_2'\text{NH}_2^+$

**Summary of reaction of amide:****(C) Esters****Methods of Preparation**

Alcohols react with acyl chlorides by nucleophilic acyl substitution to yield esters. These reactions are typically performed in the presence of a weak base such as pyridine.



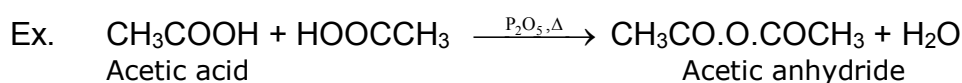
### Summary of reaction of esters :



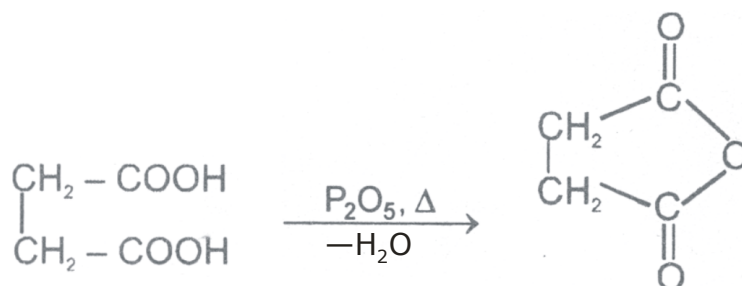
### (D) Acid anhydrides

#### Methods of Preparation of acid anhydrides

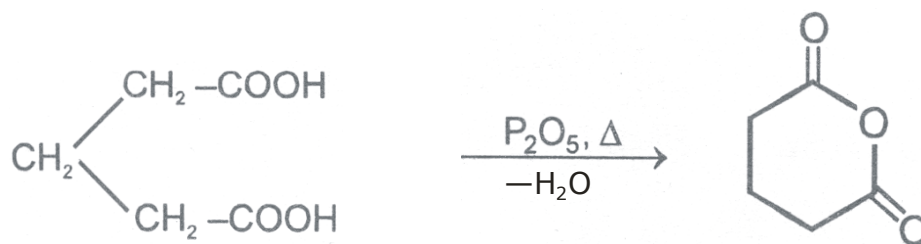
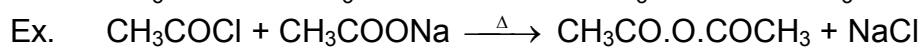
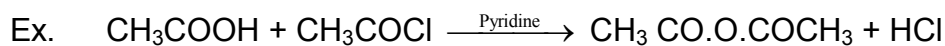
##### 1. From carboxylic acids



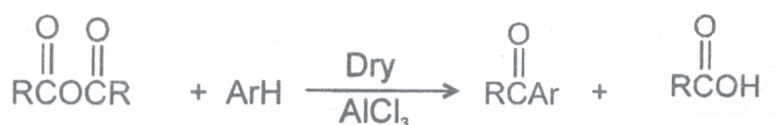
Ex.



Ex.

**2. From acid and acid halide****Chemical Reactions**

(1) Reaction with aromatic compounds (Friedel crafts acylation)



(2) Reaction with alcohols

Ex.

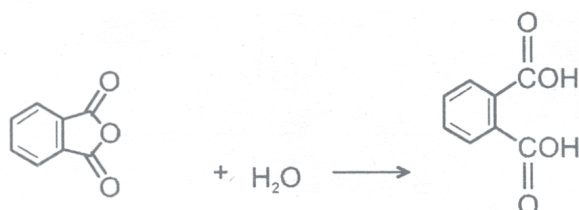


(3) Reaction with ammonia and amines

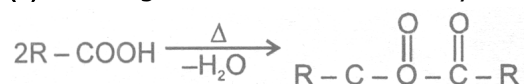


(4) Hydrolysis

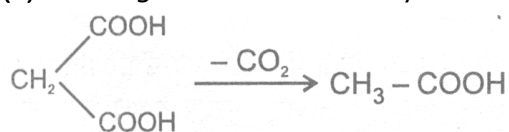
Acid anhydrides react with to yield two carboxylic. Cyclic anhydrides yield dicarboxylic acids.

**5. Heating Effects :**

(a) Heating effect on monocarboxylic acid



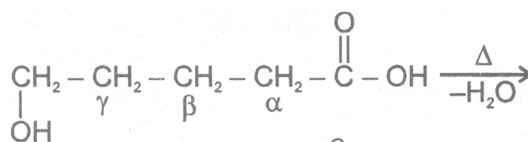
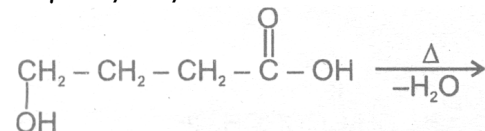
(b) Heating effect on dicarboxylic acid



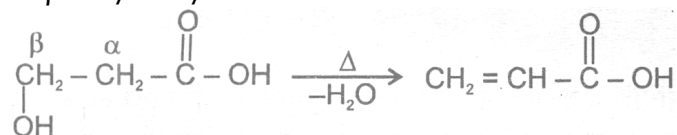
(c) Heating effect on Hydroxy acids

1.  $\delta$  - Hydroxy acid

2.  $\gamma$  - Hydroxy acid

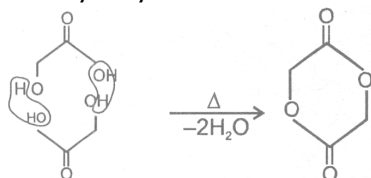


3.  $\beta$  - Hydroxy acid

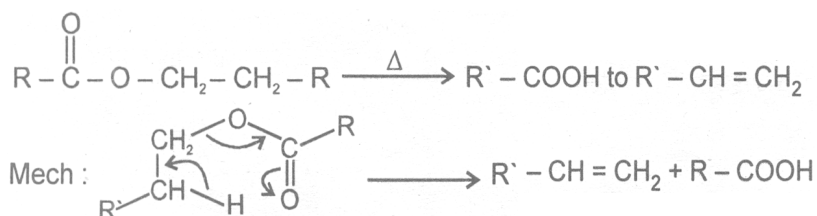


Since 4 or 8 membered rings are less stable the refore  $\beta$ -Hydroxy acids on heating produce  $\alpha, \beta$  unsaturated carboxylic acid.

4.  $\alpha$  -Hydroxy acid



• Heating effect on esters

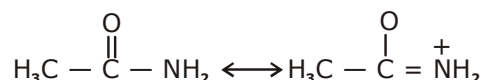


This reaction follows syn elimination & hoffman product is formes.

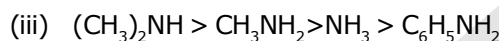
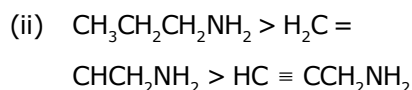
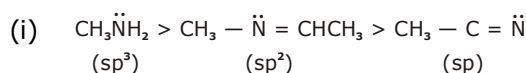
## AMINES

### 1. BASIC NATURE OF AMINES

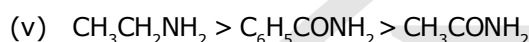
1. Aniline is less basic than ammonia. The phenyl group exerts -I (inductive effect, i.e., it withdraws electrons. This results to the lower availability of electrons on nitrogen for protonation.
2. Ethylamine and acetamide both contain an amino group but acetamide does not show basic nature. This is because lone pair of electrons on nitrogen is delocalized by resonance with the carbonyl group which makes it less available for protonation.



3. The compound with least 's' character ( $\text{sp}^3$  hybridized) is most basic and with more 's' character ( $\text{sp}$ -hybridized) is least basic. Examples in decreasing order of basicity are :



Electron withdrawing ( $\text{C}_6\text{H}_5-$ ) groups cause decrease in electron density on nitrogen atom and thereby decreasing basicity.



### 2. METHODS OF PREPARATION

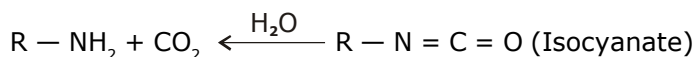
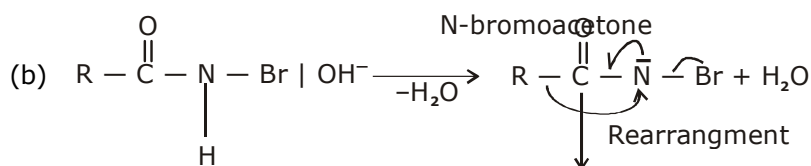
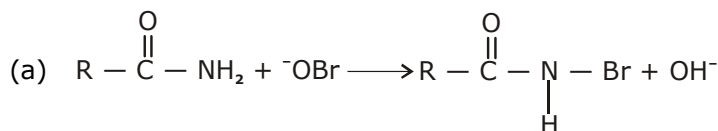
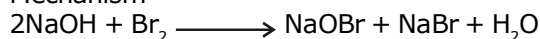
**1. Hofmann's bromamide reaction :** Amines (only primary) can also be prepared by Hoffmann degradation. In this method the amine will have one carbon atom less than the amide. The reaction proceeds via formation of nitrene.



**Mechanism of above reaction has been proposed as given below :**



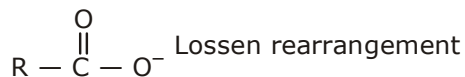
Mechanism





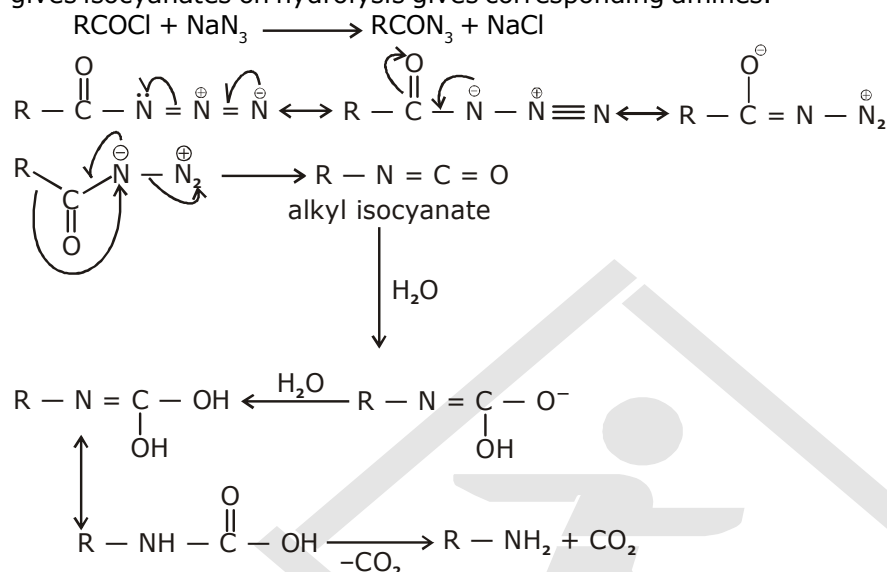
**2. Curtius, Schmidt and Lossen Rearrangement :** These reaction are basically rearrangement reaction in which carbon migrates from carbon to nitrogen with the formation of an isocyanate. In these migration i.e., 1, 2 shift, migrating group is an alkyl or aryl group and leaving group may be

- Br in Hoffmann rearrangement
- N<sub>2</sub> in Curtius and Schmidt rearrangement

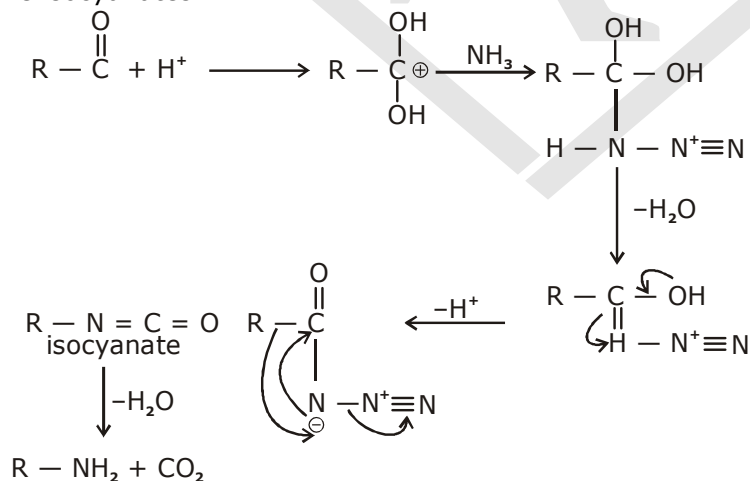


The isocyanate formed on hydrolysis gives amine.

(a) Curtius Reaction : Acid chloride on treatment with sodium azide give acid azides which on pyrolysis gives isocyanates on hydrolysis gives corresponding amines.

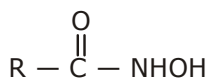


(b) Schmidt Reaction : Carboxylic acid reacts with hydrazoic acid in presence of concentrated H<sub>2</sub>SO<sub>4</sub> to give isocyanates.

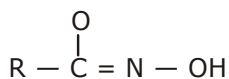


(c) Lossen Reaction : Hydroxylamine on treatment with acid chloride gives acyl derivatives of hydroxylamine the acyl derivatives exist in two tautomeric form keto form called hydroxamic form and enol form called hydroxamic acid. The hydroxamic form.



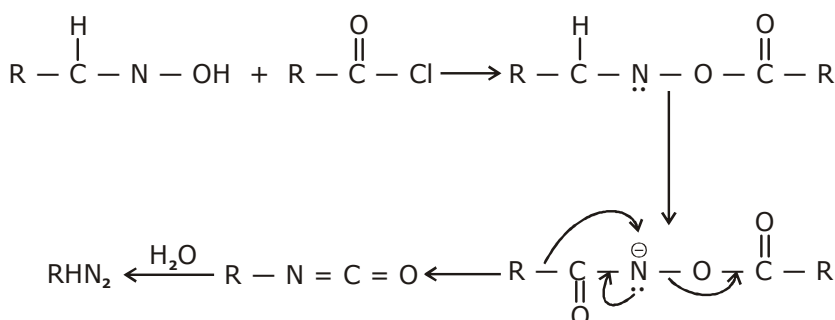


Keto form the  
hydroxamic form

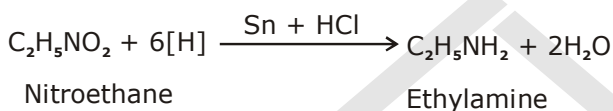


The hydroxamic  
form (enol form)

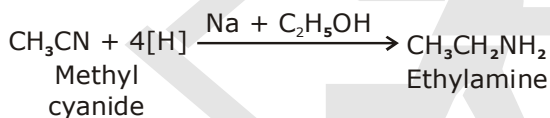
The hydroxamic form (keto form) forms o-acyl derivatives of hydroxamic form which on heating with bases forms isocyanates and finally amines upon hydrolysis.



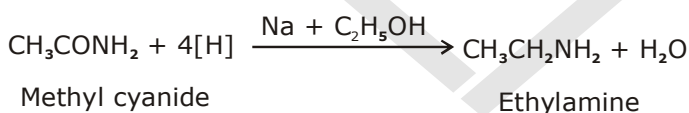
### 3. By reduction of nitroethane :



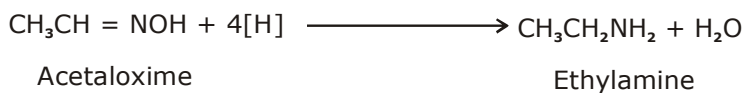
### 4. By reduction of methyl cyanide :



**5. By reduction of acetamide :** Ethylamine is obtained by reduction of acetamide with sodium and absolute alcohol or  $\text{LiAlH}_4$  in ether or hydrogen in presence of nickel catalyst.



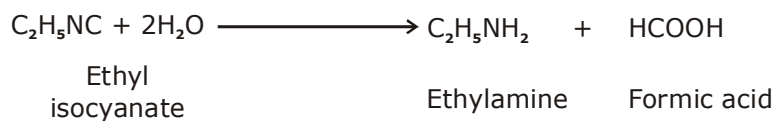
**6. By reduction of aldoxime :** Aldoxime on reduction with hydrogen and nickel catalyst or sodium and absolute alcohol or  $\text{LiAlH}_4$  in ether yields ethylamine.



**7. By the hydrolysis of ethyl isocyanate :** Ethyl isocyanate on heating with caustic potash solution undergoes hydrolysis forming ethylamine.



**8. By the acid hydrolysis of ethyl isocyanide :** Ethyl isocyanide undergoes hydrolysis with a mineral acid and forms ethylamine.



**9. By Schmidt reaction :**

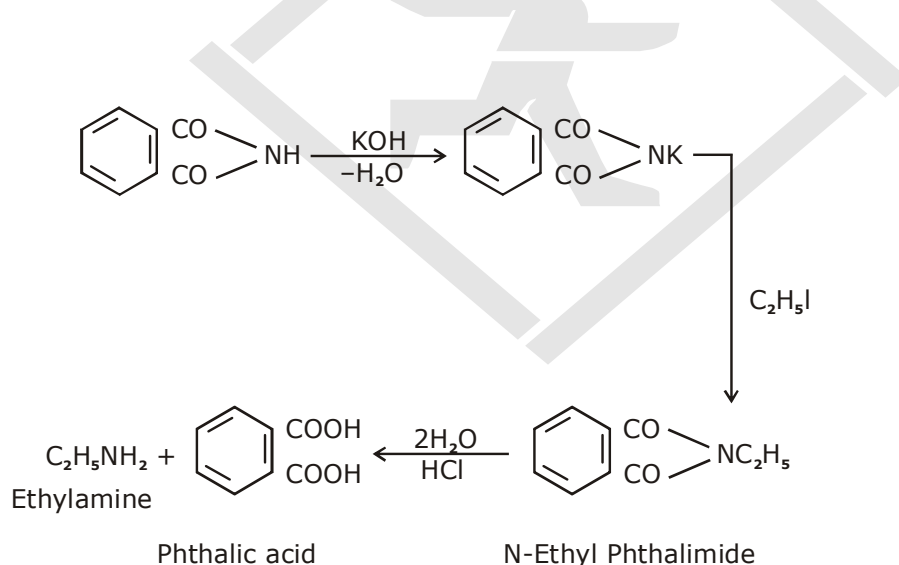


In this reaction the acyl azide  $(\text{RCON})_2$  and alkyl isocyanate  $(\text{R}-\text{NCO})$  are formed as an intermediate.

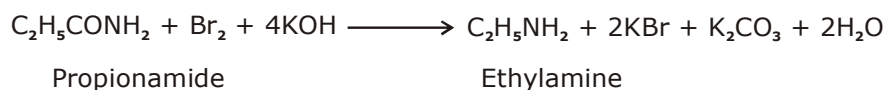
**10. By the action of chloramine on Grignard reagent :** When chloramine reacts with ethyl magnesium iodide, the formation of ethylamine occurs.



**11. By Gabriel's phthalimide reaction :**



**12. Laboratory preparation of ethylamine :** Ethylamine is prepared in the laboratory by Hofmann's bromide reaction. Propionamide is heated with bromine and potassium hydroxide solution.



### 3. PHYSICAL PROPERTIES

- (a) It is a colourless inflammable liquid. Its boiling point is 19°C.
- (b) It has fishy ammoniacal odour.
- (c) It is highly soluble in water. Its aqueous solution is basic in nature and turns red litmus blue. The solubility in water is due to hydrogen bonding with water molecules.

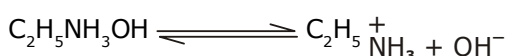
### 4. CHEMICAL PROPERTIES

(i) **Basic nature :** It is more basic than ammonia. Following reactions prove its basic nature

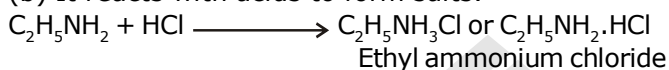
(a) It forms ethyl ammonium hydroxide when dissolved in water.



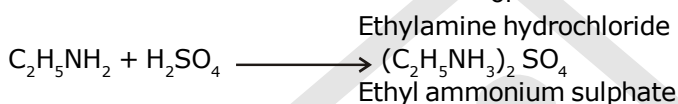
Ethyl ammonium hydroxide ionises to give  $\text{OH}^-$  ions



(b) It reacts with acids to form salts.



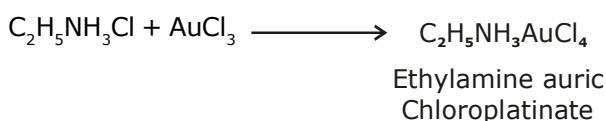
or



(c) Its aqueous solution behaves like ammonium hydroxide. The aqueous solution of ethylamine precipitates iron, chromium and aluminium as hydroxides when salts are treated with it.



(d) Its hydrochloride, like ammonium chloride, forms double salts with  $\text{PtCl}_4$  and  $\text{AuCl}_3$



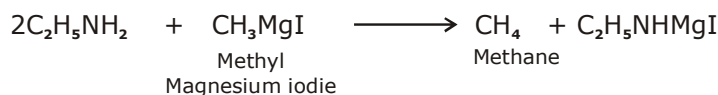
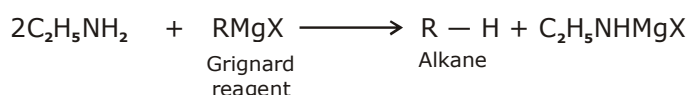
These double salts decompose on heating to pure metal and this method is used to determine the molecular mass of amines.

(ii) **Reaction with alkyl halides (Alkylation) :**

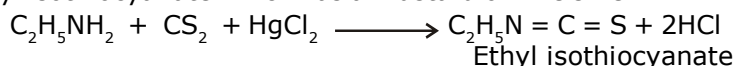
Ethylamine reacts with alkyl halides and forms secondary, tertiary amines and quaternary ammonium salt.



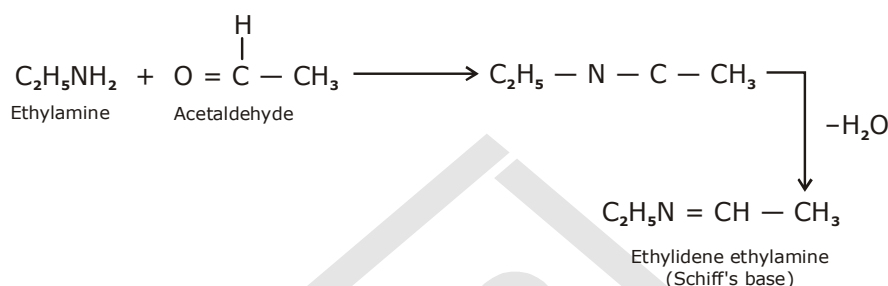
**(vi) Reaction with Grignard reagents :** Ethylamine reacts with Grignard reagents to form alkanes.



**(vii) Hofmann's mustard oil reaction :** Carbon disulphide reacts with ethylamine in presence  $\text{HgCl}_2$  to form ethyl isothiocyanate which has a mustard oil like smell.



**(viii) Reaction with aldehydes :** Ethylamine reacts additively with aldehydes to form  $\alpha$ -hydroxyl amines which are changed to Schiff bases with the elimination of water molecule.



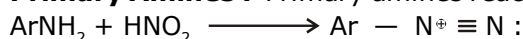
#### DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY AMINES

Test	Primary amine	Secondary amine	Tertiary amine
1. Action Test $\text{CHCl}_3$ and alcoholic KOH.	Bad smelling carbyl-amine (Isocyanide is formed)	No action.	No action.
2. Action of $\text{CS}_2$ and $\text{HgCl}_2$ . (Mustard Oil test)	Alkyl isothiocyanate is formed which has pungest smell like mustard oil.	No action.	No action.
3. Action of Nitrous acid.	Alcohol is formed with evolution of nitrogen.	Forms nitrosoamine which gives green colour with phenol and conc. $\text{H}_2\text{SO}_4$ (Liebermann's test.)	Forms nitrite in cold which on heating gives nitrosoamine which responds to Liebermann's test.
4. Action of acetyl chloride.	Acetyl derivative is formed	Acetyl derivative is formed	No action.
5. Action of Hinsberg's reagent	Monoalkyl sulphon-amide is formed which is soluble in KOH.	Dialkyl sulphonamide is formed which is insoluble in KOH.	No action.
6. Action of methyl iodide.	3 molecules (moles) of $\text{CH}_3\text{I}$ to form quaternary salt with one mole of primary amine.	2 moles of $\text{CH}_3\text{I}$ to form quaternary salt with one mole of secondary amine.	One mole of $\text{CH}_3\text{I}$ to form quaternary salt with one mole of tertiary amine.

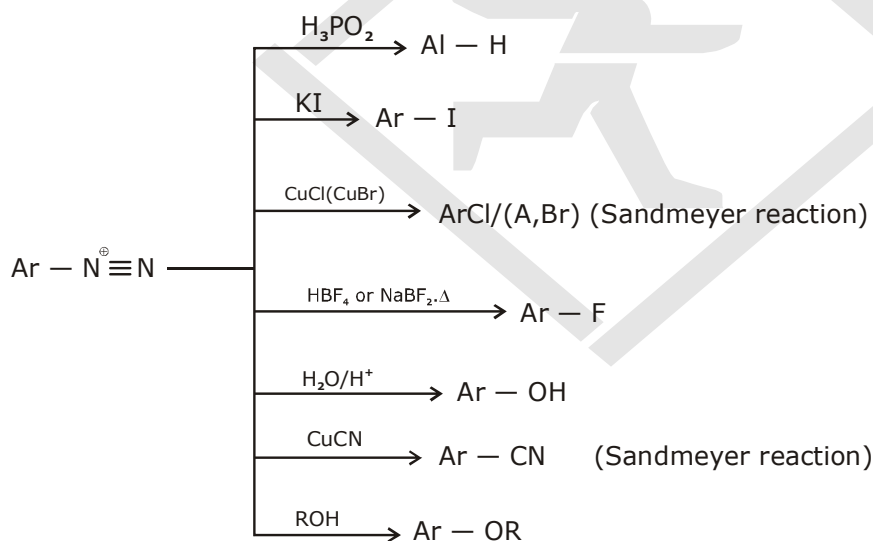
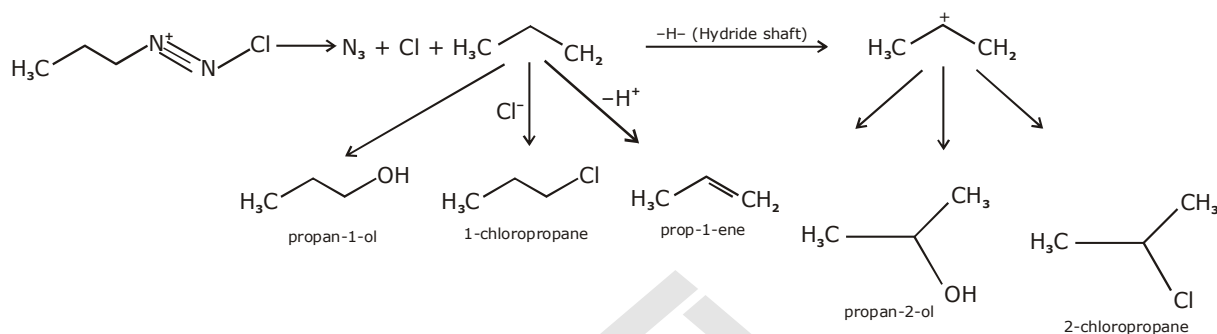
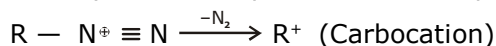
## 5. GENERAL CHEMICAL PROPERTIES OF AROMATIC AMINES

### 5.1 REACTION WITH NITROUS ACID

**1. Primary Amines :** Primary amines react with nitrous acid to produce diazonium ion as follows.



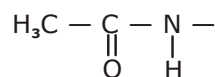
But the diazonium ions of aliphatic amines are very unstable and produces carbocation immediately, which can produce different products.



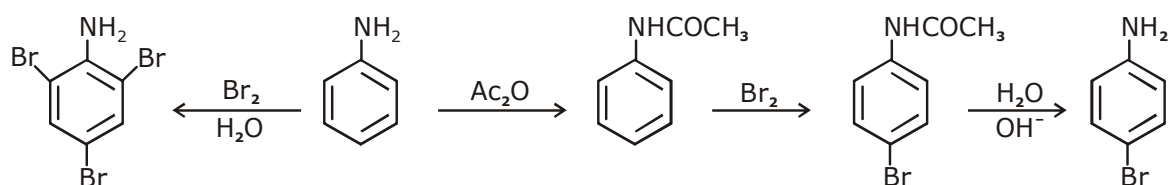
## 6. RING REACTIONS OF AROMATIC AMINES

$\text{NH}_2$  —  $\text{NHR}$  and  $-\text{NR}_2$  strongly activate the benzene ring toward electrophilic substitution

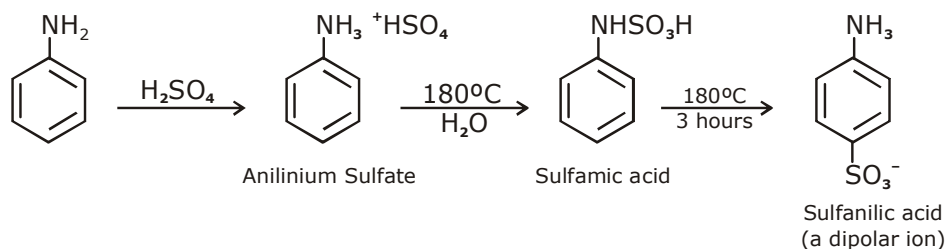
**1. Haogenation :** For monohalogenation,  $-\text{NH}_2$  is first acetylated, because



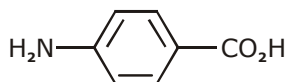
is only moderately activating and is o and p-director in nature



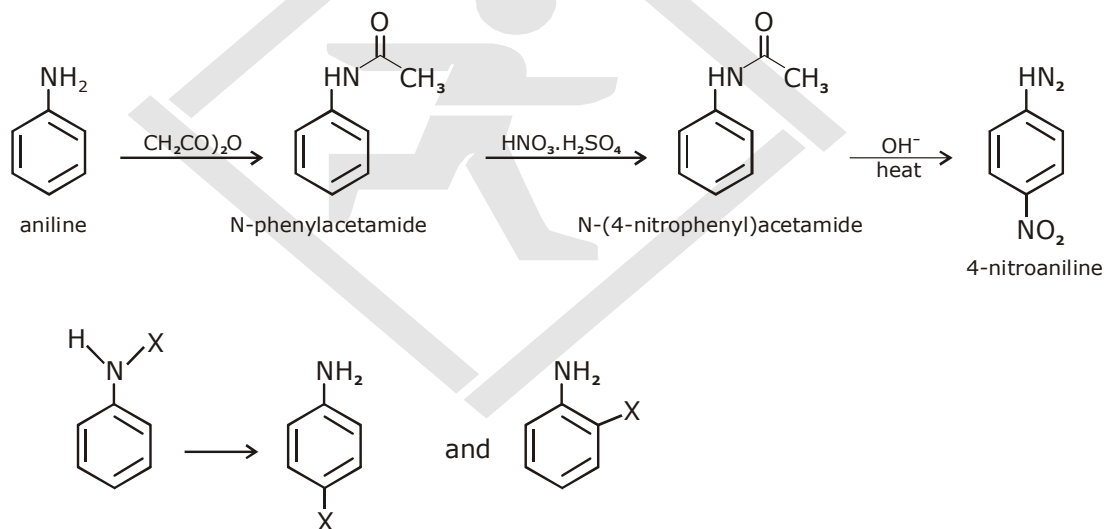
## 2. Sulfonation :



The dipolar ion structure of sulfanilic acid account for its (a) high melting point, (b) insolubility in  $H_2O$  and organic solvents, (c) solubility in aqueous NaOH, (d) insolubility in aqueous HCl.



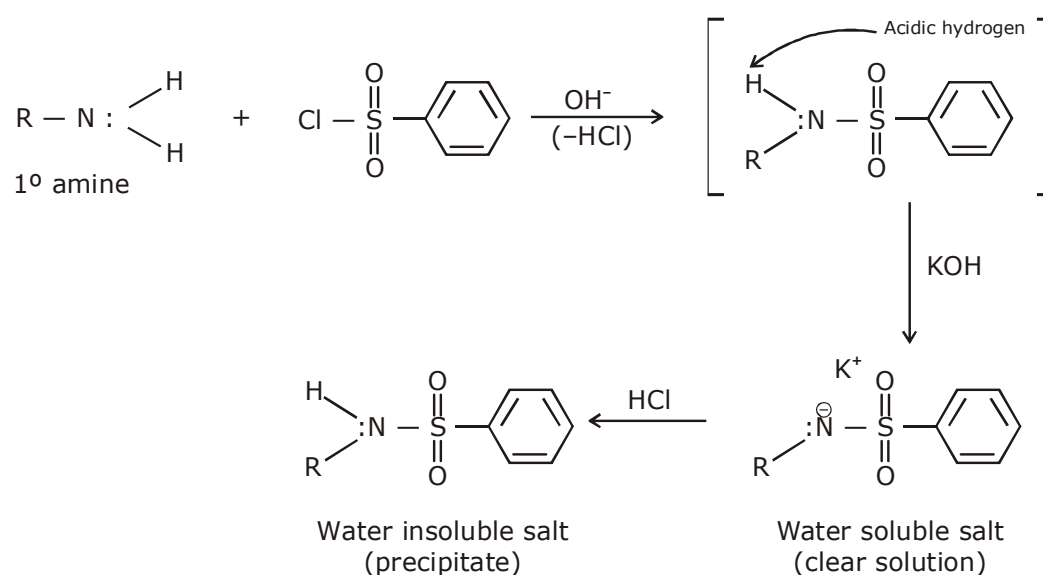
will not exists as a dipolar ino since,  $-COOH$  is too weakly acidic to transfer an  $H^+$  to the weakly basic  $-NH_2$  attached to the electron withdrawing benzene ring. When attached to an aliphatic C, the  $NH_2$  is sufficiently basic to accept  $H^-$  from  $COOH$ .



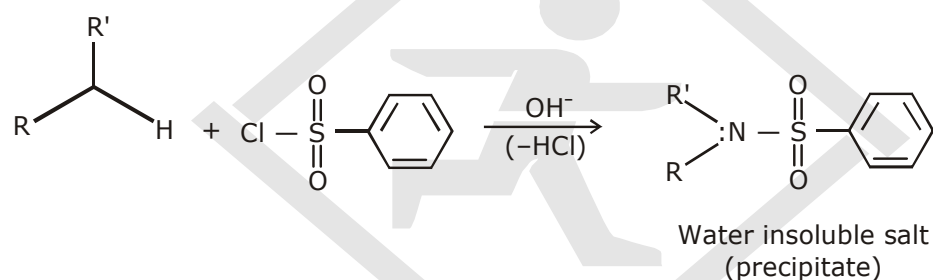
### (i) The Hinsberg Test

This test can be used to demonstrate whether an amine is primary, secondary or tertiary. Primary amines react with benzenesulfonyl chloride to form N-substituted benzenesulfonamides. These, in turn, undergo acid-base reactions with the excess potassium hydroxide to form water-soluble potassium salt. Acidification of this solution will, cause the water-soluble in the next stage, cause the water-insoluble N-substituted sulfonamide to precipitate.





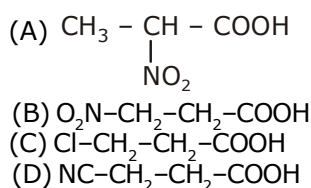
Secondary amines react with benzenesulfonyl chloride in aqueous potassium hydroxide to form insoluble, N - N-disubstituted sulfonamides that precipitate after the first stage. N<sub>3</sub>N-Disubstituted sulfonamides do not dissolve in aqueous potassium hydroxide.



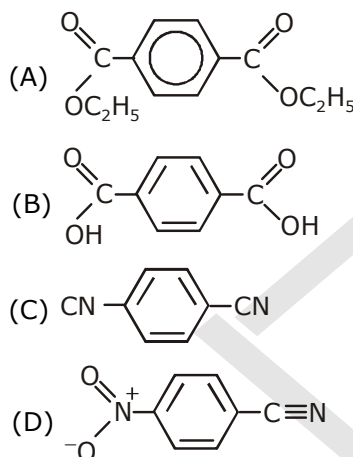
If the amine is a tertiary amine and if it is water insoluble, no apparent change will take place in the mixture as we shake it with benzenesulfonyl chloride and aqueous KOH. When we acidify the mixture, the tertiary amine dissolves because it forms a water soluble salt.

**EXERCISE – I****OBJECTIVE PROBLEMS (JEE MAIN)**

1. Which of the following acids has the smallest dissociation constant ?

**Sol.**

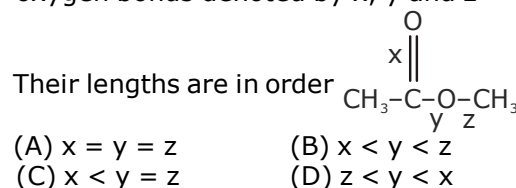
2. Which compound should have zero dipole moment ?

**Sol.**

3. When picric acid is treated with aqueous sodium bicarbonate ( $\text{NaH}^{14}\text{CO}_3$ ) a gas is liberated with effervescence. The gas evolved would be :

**Sol.**

4. In the following ester there are three carbon oxygen bonds denoted by x, y and z

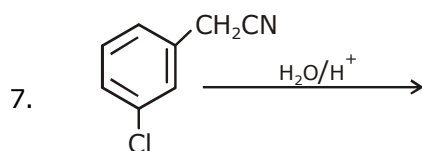
**Sol.**

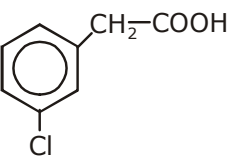
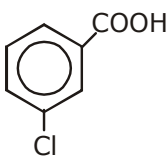
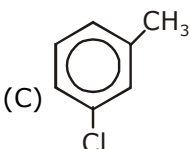
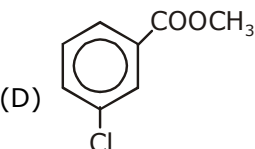
- 5.
- (C - O) bond lengths designated by A, B, C are in order :
- (A)  $A = C < B = D$  (B)  $A < B < C = D$   
 (C)  $A < C = D < B$  (D) All equal

**Sol.**

- 6.
- (A)
- (B)
- (C)
- (D)

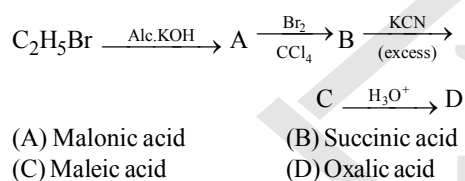
**Sol.**



- (A)  (B)   
 (C)  (D) 

Sol.

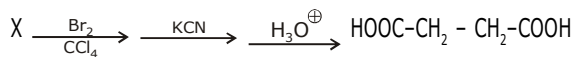
8. The acid **D** obtained through the following sequence of reactions is -



- (A) Malonic acid (B) Succinic acid  
 (C) Maleic acid (D) Oxalic acid

Sol.

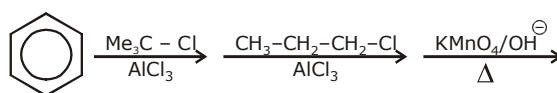
9. Identify X in the reaction sequence

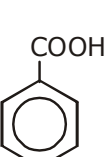
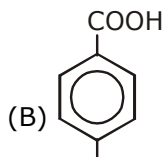
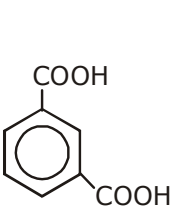
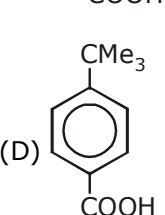


- (A)  $\text{CH}_3-\text{CH}_3$  (B)  $\text{CH}_2=\text{CH}_2$   
 (C)  $\text{H}-\text{C}\equiv\text{C}-\text{H}$  (D)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$

Sol.

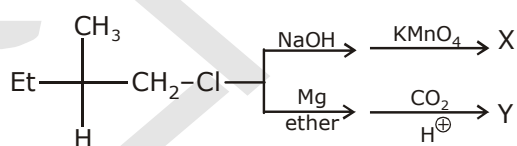
10. The final product of the following reaction sequence is



- (A)  (B)   
 (C)  (D) 

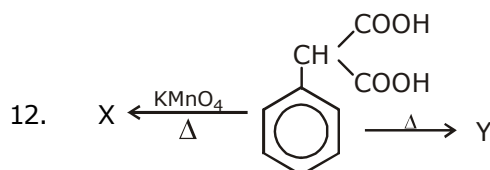
Sol.

11. In the reaction sequence X & Y are



- (A) Homologs (B) Identical  
 (C) Structural isomers (D) Enantiomers

Sol.



- In the above reaction sequence X & Y are.  
 (A) Identical (B) Homologs  
 (C) Structural isomers (D) Stereoisomers

Sol.

13. A racemic mixture of carboxylic acid having one chiral centre is treated with enantiomerically pure amine. the products formed are :  
 (A) diastereomers (both optically active)  
 (B) diastereomers (only one is optically active)  
 (C) Racemic mixture  
 (D) two optically inactive ammonium salts of acid.

Sol.

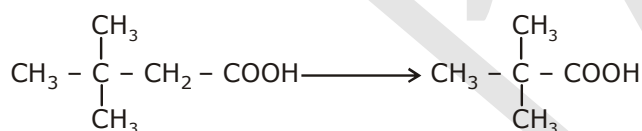
14. The product of the following reaction is



- (A)  $\text{CH}_3\text{-COOH}$  (B)  $\text{CH}_3\text{-CH}_2\text{-COOH}^{14}$   
 (C)  $\text{CH}_3\text{-COOH}^{14}$  (D)  $\text{CH}_3\text{-CH}_2\text{-COOH}^{14}$

Sol.

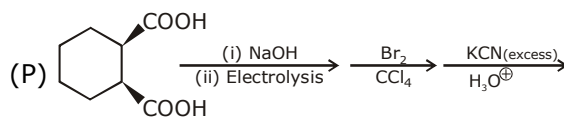
15. For the following conversion



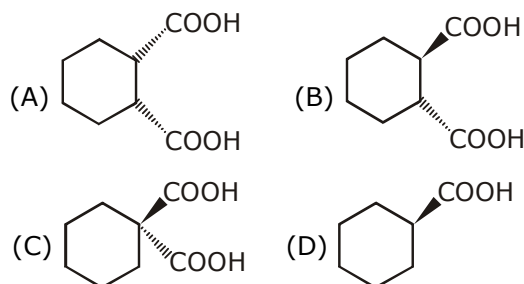
- (A)  $\xrightarrow[\Delta]{\text{NaOH/CaO}} \xrightarrow{\text{Br}_2/h\nu} \xrightarrow[\text{ether}]{\text{Mg}} \xrightarrow[(\text{ii}) \text{H}^+]{(\text{i}) \text{CO}_2}$   
 (B)  $\xrightarrow[\Delta]{\text{NaOH/CaO}} \xrightarrow{\text{Br}_2/h\nu} \xrightarrow[\text{ether}]{\text{KCN}} \xrightarrow{\text{H}_3\text{O}^+}$   
 (C)  $\xrightarrow[\Delta]{\text{NaOH/CaO}} \xrightarrow{\text{Br}_2/h\nu} \xrightarrow[\text{ether}]{\text{KCN}} \xrightarrow[(\text{ii}) \text{H}_2\text{O}]{(\text{i}) \text{O}_2} \xrightarrow{\text{KMnO}_4/\text{OH}^-}$   
 (D)  $\xrightarrow[\Delta]{\text{NaOH/CaO}} \xrightarrow{\text{Br}_2/h\nu} \xrightarrow[(\text{ii}) \text{H}_2\text{O}]{\text{H}_2\text{O/Acetone}} \xrightarrow{\text{KMnO}_4/\text{OH}^-}$

Sol.

16.

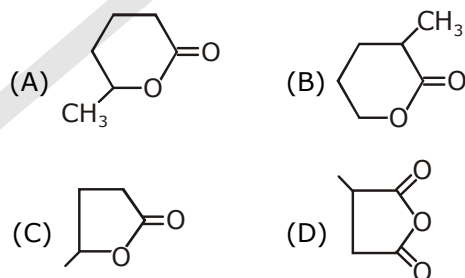


In the above reaction Q is



Sol.

17. End product of this reaction is



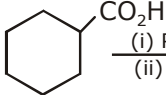
Sol.

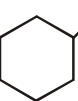
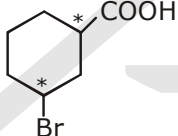
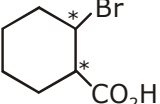

18. For the following conversion the correct sequence of reagent is



- (A)  $\xrightarrow{\text{H}_2/\text{Ni}} \xrightarrow[\Delta]{\text{H}^+}$   
 (B)  $\xrightarrow{\text{Na/LiqNH}_3} \xrightarrow[\Delta]{\text{H}^+}$   
 (C)  $\xrightarrow{\text{H}_2/\text{Pd/BaSO}_4} \xrightarrow[\Delta]{\text{H}^+}$   
 (D)  $\xrightarrow[\Delta]{\text{H}^+} \xrightarrow{\text{H}_2/\text{Pd/BaSO}_4}$

Sol.

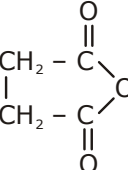
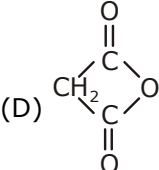
19.   $\xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) P/Br}_2}$  X, X is :

- (A)  (B)   
 (C)  (D) 

Sol.

20. In the given reaction  
 $\text{CH}_3\text{COOH} \xrightarrow[\text{(iii) H}_2\text{O/H}/\Delta]{\text{(i) Br}_2/\text{P}, \text{(ii) NaCN}^\oplus}$  [x], [x] will be

- (A)  $\text{CH}_3\text{-COOH}$   
 (B)  $\text{HOOC-CH}_2\text{-CH}_2\text{-COOH}$

- (C)  (D) 

Sol.

21. In the reaction sequence  $\text{CH}_3\text{-CH}_2\text{-COOH} \xrightarrow{\text{Br}_2/\text{PBr}_3} \text{x} \xrightarrow{\text{Br}_2} \text{y} \xrightarrow{\text{H}_2\text{O}}$

(A) x is  $\text{CH}_3 - \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{Br}$

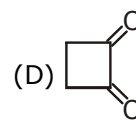
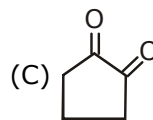
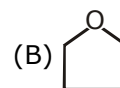
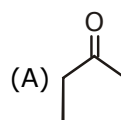
(B) y is  $\text{CH}_3 - \underset{\text{Br}}{\text{CH}} - \overset{\text{O}}{\parallel} \text{C} - \text{Br}$

(C) z is  $\text{CH}_3 - \underset{\text{Br}}{\text{CH}} - \overset{\text{O}}{\parallel} \text{C} - \text{OH}$

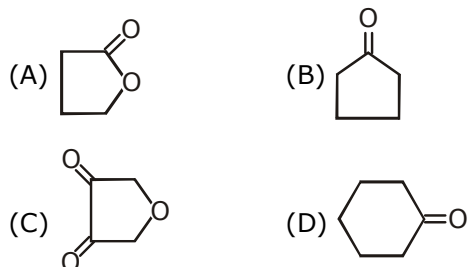
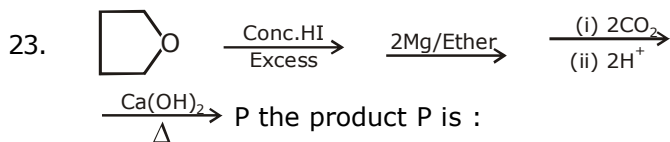
(D) All are correct

Sol.

22.  $\begin{matrix} \text{CH}_2 - \text{CH}_2\text{COO} \\ | \\ \text{CH}_2 - \text{CH}_2\text{COO} \end{matrix} \text{Ca} \xrightarrow{\Delta} \text{A, A is :}$

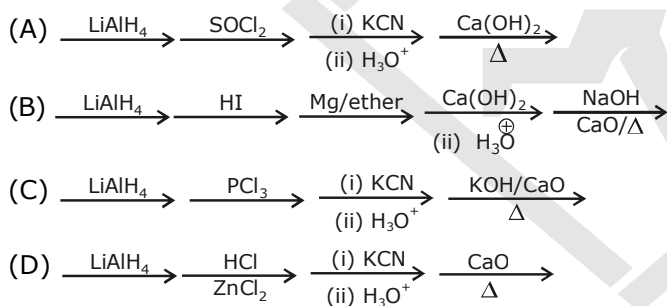
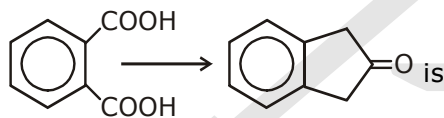


Sol.

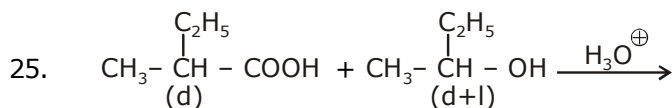


Sol.

24. The correct sequence of reagent for the following conversion.



Sol.

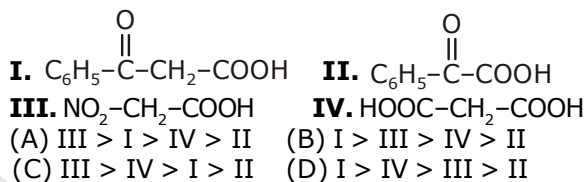


x + y the organic products x and y are :

- (A) Enantiomers (B) Diastereomers  
 (C) Metamers (D) Achiral molecules

Sol.

26. For the following acids the rate of decarboxylation on heating would be :



Sol.

## EXERCISE – II

## OBJECTIVE PROBLEMS (JEE ADVANCED)

1. Nucleophilic substitution at acyl carbon of a carboxylic acid derivative generally proceeds by.

(A) Addition-elimination mechanism  
(B) Elimination-addition mechanism  
(C)  $S_N1$  mechanism  
(D)  $S_N2$  mechanism

**Sol.**

2. The correct order of decreasing reactivity of the given compound towards hydrolysis under identical condition is:

(A)  $\text{CH}_3\text{COCl} > \text{CH}_3\text{CONH}_2 > (\text{CH}_3\text{CO})_2\text{O} > \text{CH}_3\text{COOCH}_3$   
(B)  $\text{CH}_3\text{COCl} > (\text{CH}_3\text{CO})_2\text{O} > \text{CH}_3\text{COOCH}_3 > \text{CH}_3\text{CONH}_2$   
(C)  $\text{CH}_3\text{COOCH}_3 > \text{CH}_3\text{COCl} > (\text{CH}_3\text{CO})_2\text{O} > \text{CH}_3\text{CONH}_2$   
(D)  $(\text{CH}_3\text{CO})_2\text{O} > \text{CH}_3\text{COCl} > \text{CH}_3\text{COOCH}_3 > \text{CH}_3\text{CONH}_2$

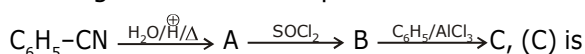
**Sol.**

3. Which of the following proposed reactions would take place most quickly under mild conditions ?

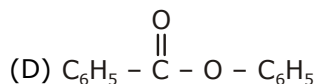
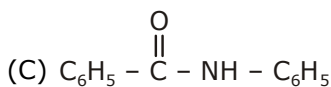
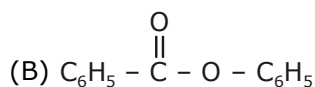
(A)  $\text{CH}_3\text{-CO-NH}_2 + \text{NaCl} \rightarrow \text{CH}_3\text{COCl} + \text{NaNH}_2$   
(B)  $\text{C}_6\text{H}_5\text{-CO-Cl} + \text{CH}_3\text{NH}_2 \rightarrow \text{C}_6\text{H}_5\text{-C(=O)-NH-CH}_3$   
(C)  $\text{CH}_3\text{-CO-Cl} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{-CO-NH-CH}_3$   
(D)  $\text{CH}_3\text{-COO-C}_2\text{H}_5 + \text{HOH} \xrightarrow{\text{NaOH}} \text{CH}_3\text{-COONa} + \text{C}_2\text{H}_5\text{OH}$

**Sol.**

4. In the given reaction sequence :

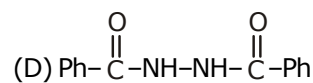
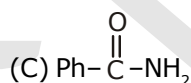
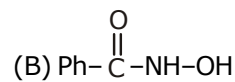
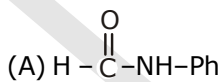


(A)  $\text{C}_6\text{H}_5\text{-C(=O)-C}_6\text{H}_5$



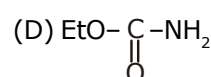
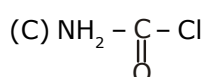
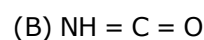
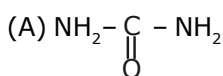
**Sol.**

5.  $\text{H}_2\text{N-NH}_2 + \text{Ph-C(=O)-Cl (excess)} \xrightarrow{\text{NaOH}} \text{X, X is}$



**Sol.**

6. Phosgene( $\text{COCl}_2$ ) + 1 mol  $\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{NH}_3}$  X, X is

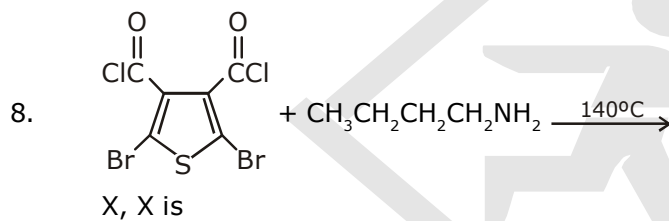


**Sol.**

7.  $\text{CH}_3\text{O-C}_6\text{H}_4\text{-C(=O)-Cl} + \text{C}_6\text{H}_5\text{-C(=O)-CH(OH)-C}_6\text{H}_5 \xrightarrow{\text{Pyridine}}$  X, X is

- (A)  $\text{Ph} - \text{O} - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{O} - \text{CH}(\text{CH}_3) - \text{C}(=\text{O}) - \text{H}$
- (B)  $\text{Ph} - \text{O} - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{O} - \text{CH}(\text{CH}_3) - \text{C}(=\text{O}) - \text{H}$
- (C)  $\text{CH}_3 - \text{O} - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{O} - \text{CH}(\text{Ph}) - \text{C}(=\text{O}) - \text{Ph}$
- (D)  $\text{Ph} - \text{O} - \text{C}_6\text{H}_4 - \text{C}(=\text{O}) - \text{O} - \text{CH}(\text{CH}_3) - \text{C}(=\text{O}) - \text{Ph}$

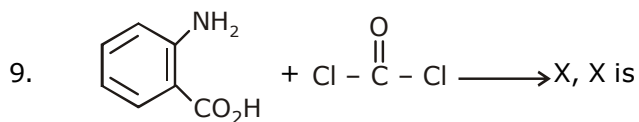
Sol.



- (A)  $\text{CH}_3 - \text{CH}(\text{CH}_2\text{CH}_3) - \text{N}(\text{C}_4\text{H}_2\text{Br}_2) - \text{CH}_2 - \text{CH}_3$
- (B)  $\text{CH}_3 - \text{C}(\text{CH}_3)_2 - \text{N}(\text{C}_4\text{H}_2\text{Br}_2) - \text{CH}_2 - \text{CH}_3$

- (C)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 - \text{N}(\text{C}_4\text{H}_2\text{Br}_2) - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
- (D)  $\text{CH}_3 - \text{CH}(\text{CH}_2\text{CH}_3) - \text{N}(\text{C}_4\text{H}_2\text{Br}_2) - \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

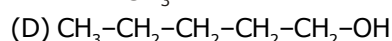
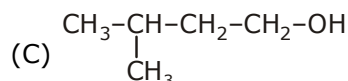
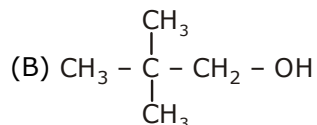
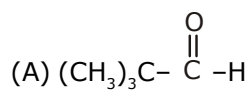
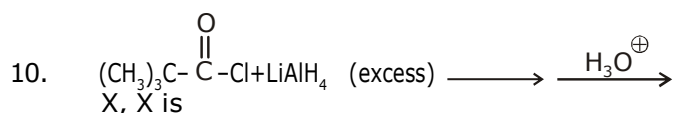
Sol.



- (A)  $\text{C}_6\text{H}_4(\text{NH} - \text{C}(=\text{O}) - \text{Cl})(\text{COOH})$
- (B)  $\text{C}_6\text{H}_4(\text{N}=\text{C}(\text{OH})\text{O})(\text{CH}(\text{OH})_2)$
- (C)  $\text{C}_6\text{H}_4(\text{NH} - \text{O} - \text{C}(=\text{O}) - \text{O})(\text{CH}(\text{OH})_2)$
- (D)  $\text{C}_6\text{H}_4(\text{NH} - \text{C}(=\text{O}) - \text{O})(\text{C}(=\text{O}) - \text{O})$

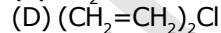
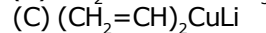
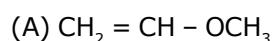
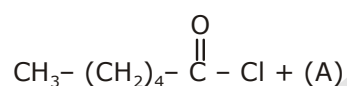
Sol.



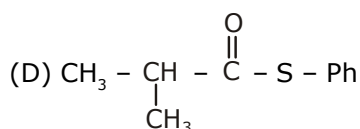
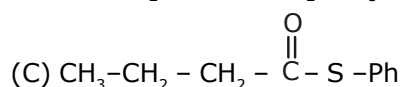
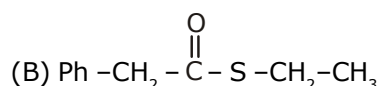
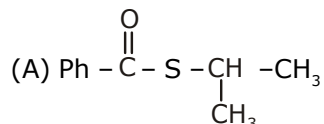
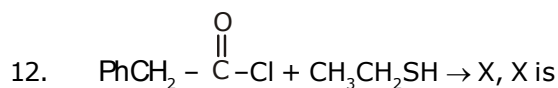


**Sol.**

11. For the given reaction

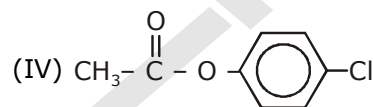
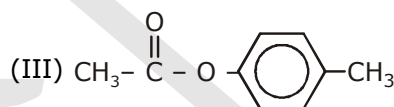
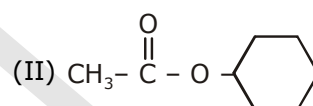
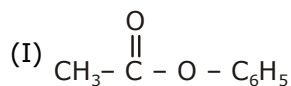


**Sol.**



**Sol.**

13. List the following esters in order of decreasing reactivity in the second step of a nucleophilic acyl substitution reaction.



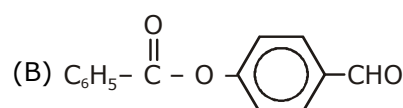
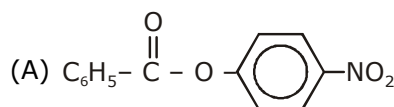
Select the correct answer from the codes given below:

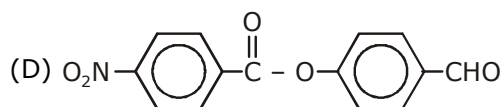
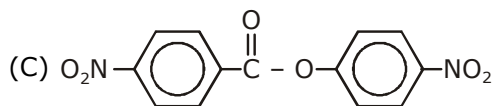
(A) IV > I > III > II (B) IV > III > I > II

(C) III > IV > I > II (D) II > I > III > IV

**Sol.**

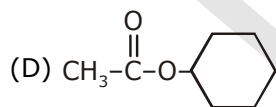
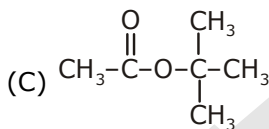
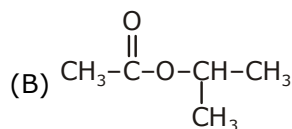
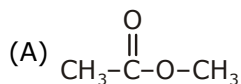
14. Which one of the following is least reactive for hydrolysis reaction?





Sol.

15. Which one of the following esters is most reactive for saponification ?



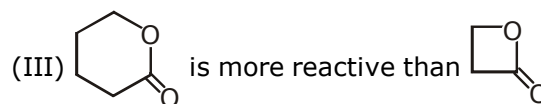
Sol.

16. Consider the following statements for hydrolysis reaction :

(I) is more reactive than  $\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5$

(II) is more reactive

than



Of these the correct statements are

- (A) I and II (B) I, II and III  
(C) II and III (D) I and III

Sol.

17. Ease of esterification of following acids with  $\text{CH}_3\text{OH}$

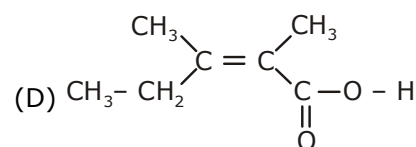
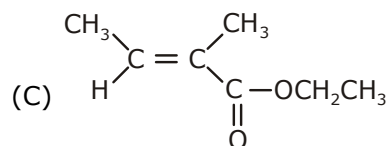
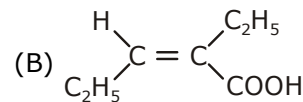
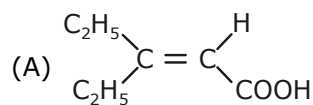
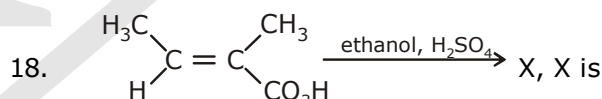
(I)  $\text{HCOOH}$  (II)  $\text{CH}_3\text{COOH}$

(III)  $\text{CH}_3-\text{CH}_2-\text{COOH}$

(IV)  $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{COOH}$ , is

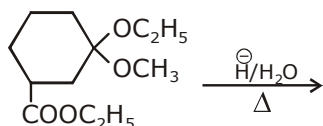
- (A)  $\text{I} = \text{II} = \text{III} = \text{IV}$  (B)  $\text{I} > \text{II} > \text{III} > \text{IV}$   
(C)  $\text{I} < \text{II} < \text{III} < \text{IV}$  (D)  $\text{I} > \text{IV} > \text{III} > \text{II}$

Sol.



Sol.

19. In the given reaction

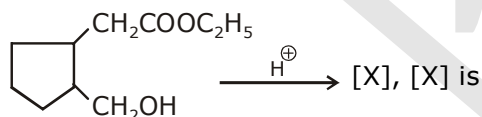


[P], [P] will be :

- (A) (B) (C) (D)

Sol.

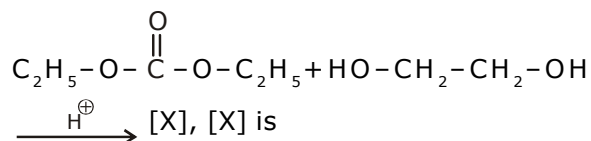
20. In the given reaction



- (A) (B) (C) (D)

Sol.

21. In the given reaction



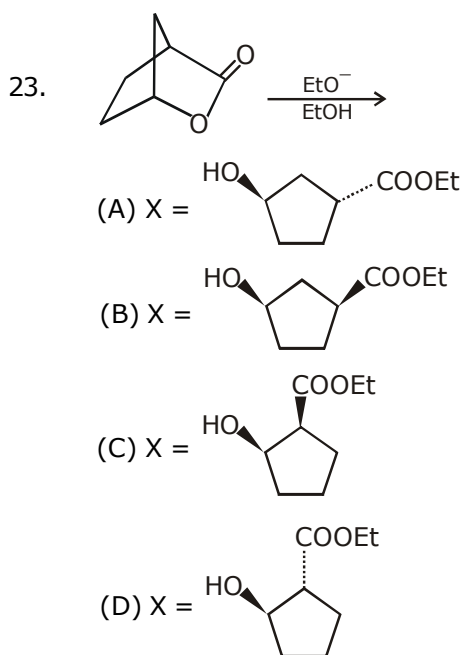
- (A)  $\text{C}_2\text{H}_5\text{O}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$   
 (B)  $\text{HO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$   
 (C)   
 (D) No reaction is possible

Sol.

22. X, X is

- (A)  $\text{H}_3\text{CO}-\text{C}(=\text{O})-(\text{CH}_2)_5\text{OH}$   
 (B)  $\text{H}_3\text{CO}-\text{C}(=\text{O})-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$   
 (C)  $\text{H}_3\text{CO}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-\text{OH}$   
 (D)  $\text{H}_3\text{CO}-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{OH}$

Sol.

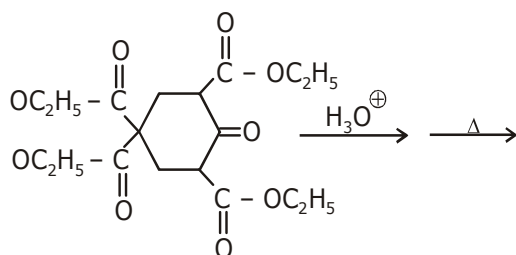


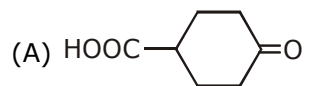
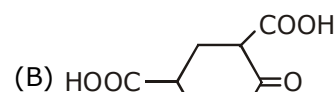
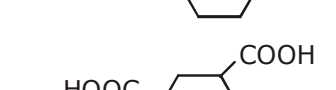
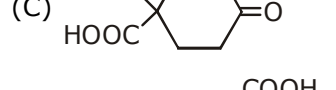
Sol.

24. Ease of esterification of following alcohol with HCOOH is  
 (I)  $\text{CH}_3\text{-CH}_2\text{OH}$  (II)  $(\text{CH}_3)_2\text{CH-OH}$   
 (III)  $(\text{CH}_3)_3\text{C-OH}$   
 (A)  $\text{III} > \text{II} > \text{I}$  (B)  $\text{I} > \text{II} > \text{III}$   
 (C)  $\text{II} > \text{I} > \text{III}$  (D)  $\text{II} > \text{III} > \text{I}$

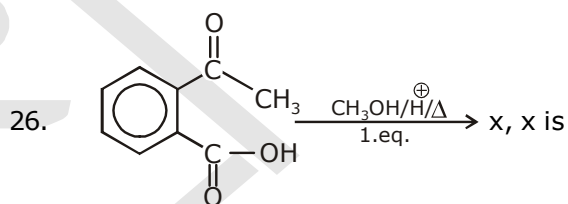
Sol.

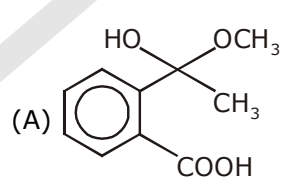
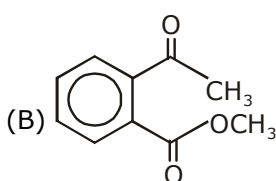
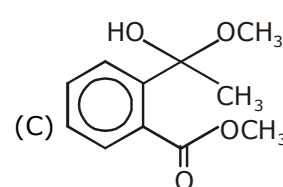
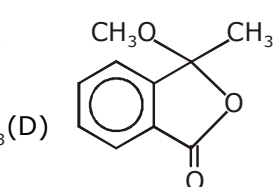
25. The product x in the above reaction is



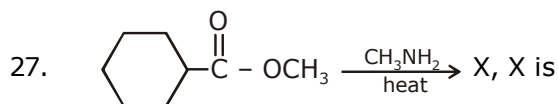
- (A) 
- (B) 
- (C) 
- (D) 

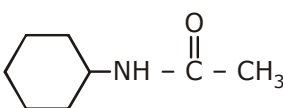
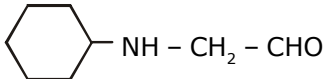
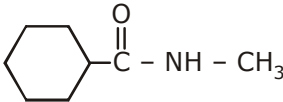
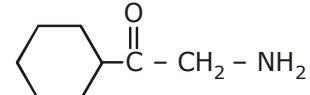
Sol.



- (A) 
- (B) 
- (C) 
- (D) 

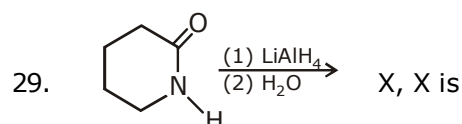
Sol.

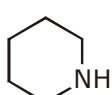
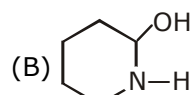
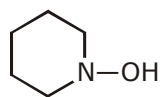
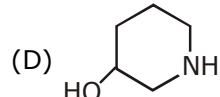


- (A)   
 (B)   
 (C)   
 (D) 

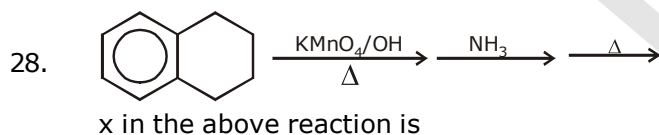
Sol.

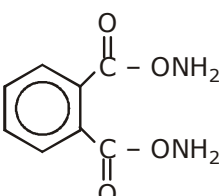
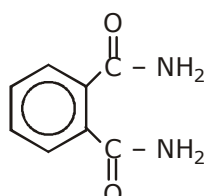
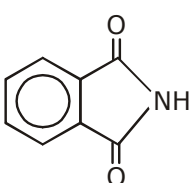
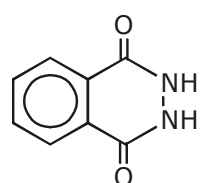
Sol.



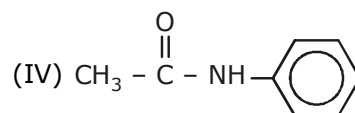
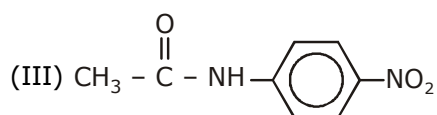
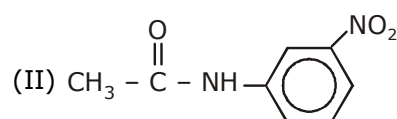
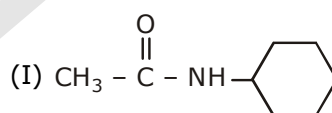
- (A)   
 (B)   
 (C)   
 (D) 

Sol.



- (A)   
 (B)   
 (C)   
 (D) 

30. Consider the following compounds :

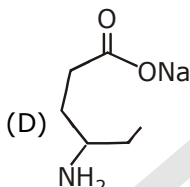
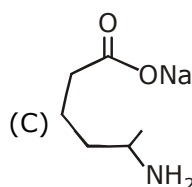
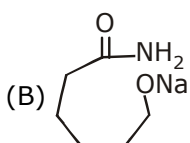
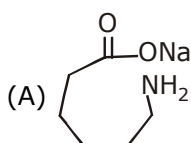
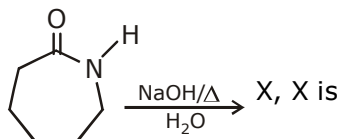


The decreasing order of reactivity towards hydrolysis by aqueous NaOH is :

- (A) I > II > III > IV (B) III > II > IV > I  
 (C) IV > I > II > III (D) I > IV > II > III

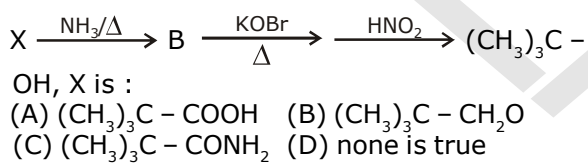
Sol.

31.



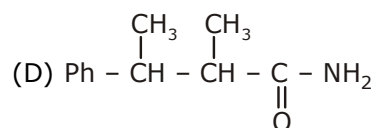
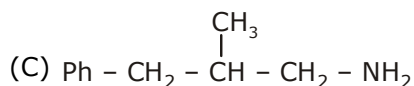
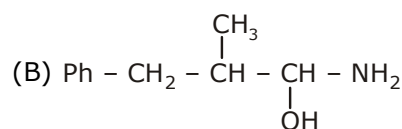
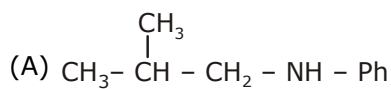
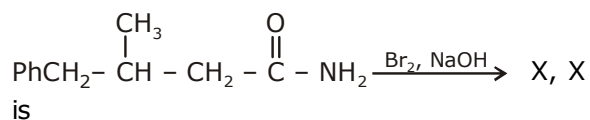
Sol.

32.



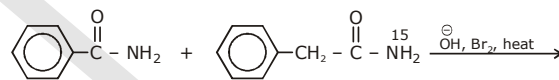
Sol.

33.

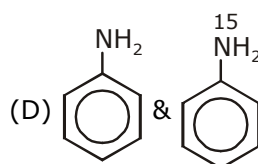
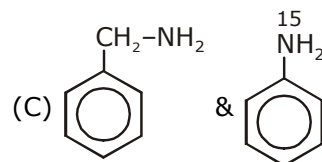
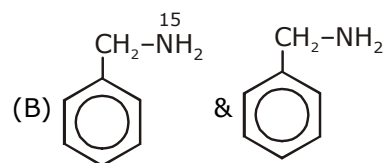
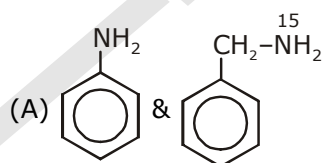


Sol.

34.



Product X & Y are :-



Sol.

35. Urea ( $\text{H}_2\text{NCONH}_2$ ) + hot dilute NaOH  $\longrightarrow$  X +  $\text{NH}_3$ , X is

- (A)  $\text{NaNH} - \text{C}(=\text{O}) - \text{NH} \cdot \text{Na}$  (B)  $\text{NH}_2 - \text{C}(=\text{O}) - \text{NH} \cdot \text{Na}$   
 (C)  $\text{Na}_2\text{CO}_3$  (D)  $\text{H} - \text{C}(=\text{O}) - \text{NH}_2$

Sol.

36. In the given reaction sequence

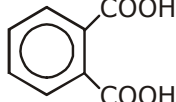


(A) and (B) respectively are :

- (A)  $\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \\ \text{C} \begin{array}{l} \text{COCl} \\ \text{COOH} \end{array} \\ \diagdown \\ \text{C}_2\text{H}_5 \end{array}$  and  $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5 - \text{C} - \text{NH} - \text{C} = \text{O} \\ \diagup \quad \diagdown \\ \text{COOH} \quad \text{NH}_2 \end{array}$   
 (B)  $\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \\ \text{C} \begin{array}{l} \text{COCl} \\ \text{COCl} \end{array} \\ \diagdown \\ \text{C}_2\text{H}_5 \end{array}$  and  $\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \\ \text{C} \begin{array}{l} \text{CO} - \text{NH} \\ \text{CO} - \text{NH} \end{array} \text{C} = \text{O} \\ \diagdown \quad \diagup \end{array}$   
 (C)  $\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \\ \text{C} \begin{array}{l} \text{COCl} \\ \text{COOH} \end{array} \\ \diagdown \\ \text{C}_2\text{H}_5 \end{array}$  and  $\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \\ \text{C} \begin{array}{l} \text{CO} - \text{NH} \\ \text{CO} - \text{NH} \end{array} \text{C} = \text{O} \\ \diagdown \quad \diagup \end{array}$   
 (D)  $\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \\ \text{C} \begin{array}{l} \text{CO} \\ \text{CO} \end{array} \\ \diagdown \\ \text{C}_2\text{H}_5 \end{array}$  and  $\begin{array}{c} \text{C}_2\text{H}_5 \\ \diagup \\ \text{C} \begin{array}{l} \text{CO} - \text{NH} \\ \text{CO} - \text{NH} \end{array} \text{C} = \text{O} \\ \diagdown \quad \diagup \end{array}$

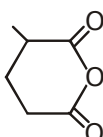
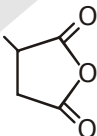
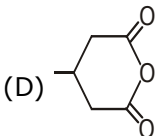
Sol.

37. Following will not yield a cyclic compound on heating :

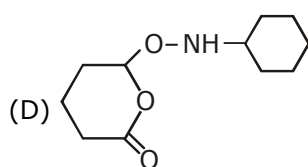
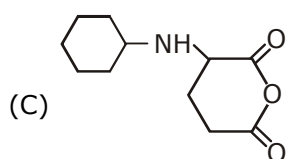
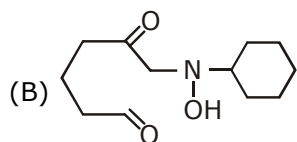
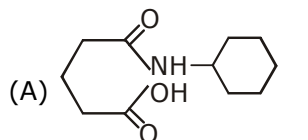
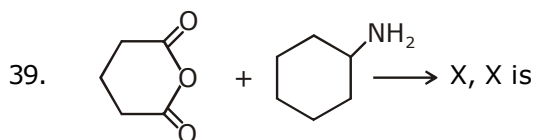
- (A)  $\begin{array}{c} \text{COOH} \\ \diagup \\ \text{CH}_2 \\ \diagdown \\ \text{COOH} \end{array}$  (B)  $\begin{array}{c} \text{CH}_2 - \text{COOH} \\ | \\ \text{CH}_2 - \text{COOH} \end{array}$   
 (C)  $\begin{array}{c} \text{CH}_2\text{COOH} \\ \diagup \quad \diagdown \\ \text{CH}_2\text{COOH} \end{array}$  (D) 

Sol.

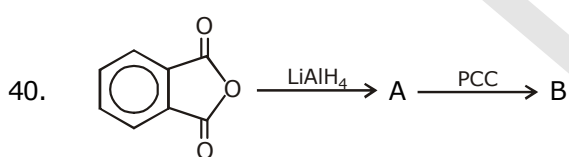
38. In the following reaction  $\text{X} \xrightarrow{\Delta} \text{Y}$ . X is the lowest molecular weight optically active dicarboxylic acid. What is the structure of Y.

- (A)  $\text{CH}_3 - \text{CH}(\text{CH}_3) - \text{COOH}$  (B)   
 (C)  (D) 

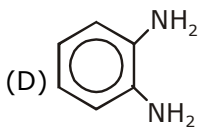
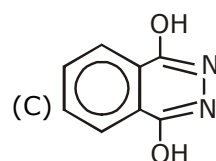
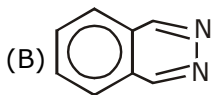
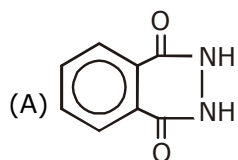
Sol.



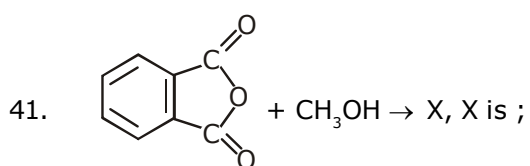
**Sol.**



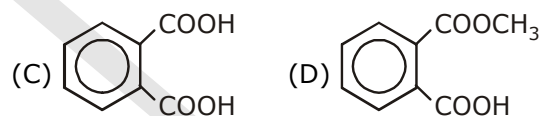
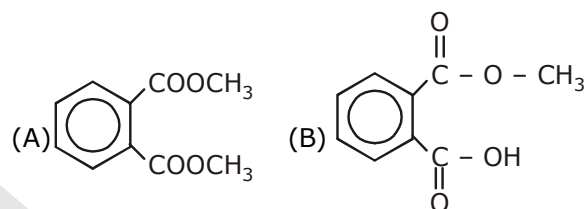
$\xrightarrow{\text{NH}_2\text{-NH}_2}$  C, Product (C) is



**Sol.**



Phthalic anhydride



**Sol.**



**EXERCISE – III****OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. The increasing order of basicity of  $\text{RCN}$ ,  $\text{RCN} = \text{NR}$  and  $\text{RHN}_2$  is  
 (A)  $\text{RCN} < \text{RCH} = \text{NR} < \text{RHN}_2$   
 (B)  $\text{RNH}_2 < \text{RCH} < \text{RCH} = \text{NR}$   
 (C)  $\text{RCN} = \text{NR} < \text{RNH}_2 < \text{RCN}$   
 (D)  $\text{RH}_2\text{N} < \text{RCH} = \text{NR} < \text{RCN}$ .

**Sol.**

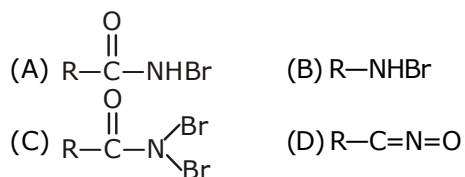
2. How many isomeric amines with that formula  $\text{C}_7\text{H}_9\text{N}$  contains a benzene ring ?  
 (A) two (B) three (C) four (D) five

**Sol.**

3. Isopropylamine can be obtained by  
 (A)  $(\text{CH}_3)_2\text{CHO} + \text{NH}_2\text{OH} \rightarrow ? \xrightarrow{\text{LiAlH}_4}$   
 (B)  $(\text{CH}_3)_2\text{CHO} + \text{NH}_3 \xrightarrow{\Delta} ? \xrightarrow{\text{H}_2/\text{Ni}}$   
 (C)  $\begin{array}{c} \text{H}_3\text{C} \\ | \\ \text{H}_3\text{C}-\text{CHOH} \end{array} + \text{NH}_3 \longrightarrow$  (D) All of these

**Sol.**

4. Reaction of  $\text{RCONH}_2$  with a mixture of  $\text{Br}_2$  and  $\text{KOH}$  gives  $\text{RNH}_2$  as the main product. The intermediate involved in the reaction is

**Sol.**

5. Amines are highly soluble in:  
 (A) Alcohol (B) Diethyl ether  
 (C) benzene (D) Water

**Sol.**

6. Which of the following reagents can convert benzene diazonium chloride into benzene ?  
 (A) Water  
 (B) Acid  
 (C) Hypophosphorous acid  
 (D)  $\text{HCl}$

**Sol.**

7. The bromination of aniline produces  
 (A) 2-bromoaniline (B) 4-bromoaniline  
 (C) 2,4,6-tribromoaniline (D) 2,6-dibromoaniline

**Sol.**

8. The compound, which on reaction with aqueous nitrous acid at low temperature produced an only nitrosoamine is  
 (A) Methyl amine (B) Ethylamine  
 (C) Diethylamine (D) Triethylamine

**Sol.**

9. Carbylamine test is performed in alcoholic  $\text{KOH}$  by heating a mixture of  
 (A) Chloroform and silver powder  
 (B) Trihalogenated methane and a primary amine  
 (C) An alkyl halide and a primary amine  
 (D) An alkyl cyanide and a primary amine

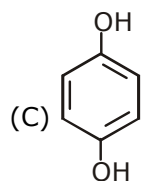
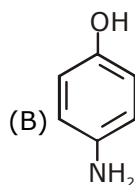
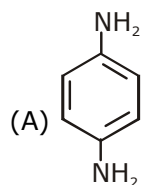
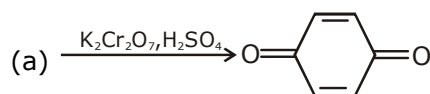
**Sol.**

10. Activation of benzene ring by  $-\text{NH}_2$  in aniline can be reduced by treating with  
 (A) Dilute  $\text{HCl}$  (B) Ethyl alcohol  
 (C) Acetic acid (D) Acetyl chloride

**Sol.**



18. Identify compound (A) in the following oxidation reaction.



(D) All of these

Sol.

19. p-Cl C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> and PhNH<sub>3</sub><sup>+</sup> Cl<sup>-</sup> can be distinguished by

(A) Ag(OH) (B) NaOH  
(C) AgNO<sub>3</sub> (D) None of these

Sol.

20. Acetamide is treated with the following reagents. Which one of these would give methylamine?

(A) PCl<sub>5</sub> (B) NaOH+Br<sub>2</sub>  
(C) soda lime (D) Hot conc. HSO<sub>4</sub>

Sol.

21. Treatment of ammonia with excess of ethyl chloride will yield

(A) diethyl amine  
(B) dethane  
(C) tetraethylammonium  
(D) methyl amine

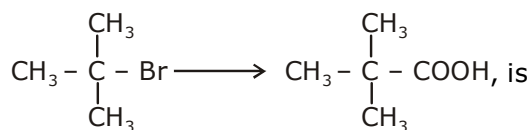
Sol.

22. C<sub>6</sub>H<sub>5</sub>C≡N and C<sub>6</sub>H<sub>5</sub>N=C exhibit which type of isomerism?

(A) Position  
(B) Functional  
(C) Dextroisomerism  
(D) Positional isomerism

Sol.

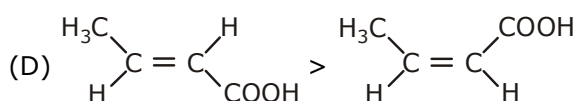
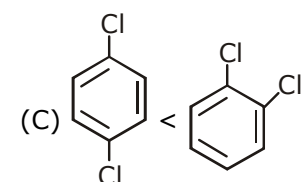
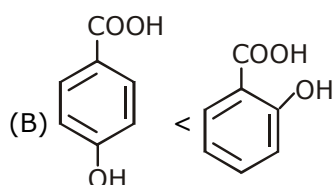
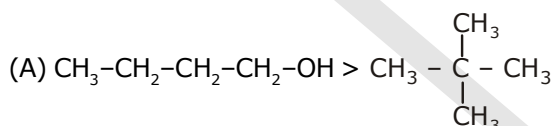
23. The correct reagent sequence for the following conversion



- (A)  $\xrightarrow{\text{KCN}} \xrightarrow[\Delta]{\text{H}_3\text{O}^+}$   
 (B)  $\xrightarrow{\text{Mg/ether}} \xrightarrow{\text{CO}_2} \xrightarrow{\text{H}^+}$   
 (C)  $\xrightarrow{\text{Mg/ether}} \xrightarrow{\text{Cl-COOH}}$   
 (D)  $\xrightarrow{\text{Mg/ether}} \xrightarrow[1.\text{eq.}]{\text{HCOCl}} \xrightarrow[1.\text{eq.}]{\text{KMnO}_4/\text{OH}^-}$

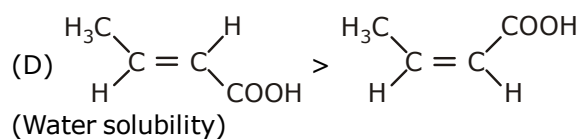
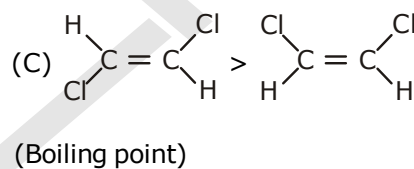
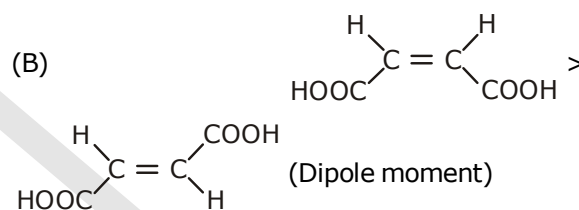
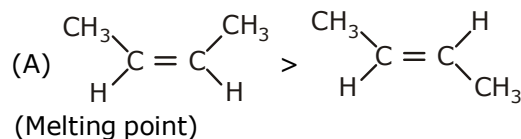
**Sol.**

24. Correct water solubility order/is amongst the following pairs is/are.



**Sol.**

25. The correct order/s for the given pair of isomers is/are



**Sol.**



**Q.6** Which one of the following does not have  $sp^2$  hybridized carbon ? **[AIEEE-2004]**

- (A) Acetone (B) Acetic acid  
(C) Acetonitrile (D) Acetamide

**Sol.**

**Q.7** Consider the acidity of the carboxylic acids : **[AIEEE-2004]**

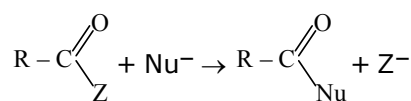
- (a)  $\text{PhCOOH}$   
(b)  $o\text{-NO}_2\text{C}_6\text{H}_4\text{COOH}$   
(c)  $p\text{-NO}_2\text{C}_6\text{H}_4\text{COOH}$   
(d)  $m\text{-NO}_2\text{C}_6\text{H}_4\text{COOH}$

Which of the following order is correct ?

- (A)  $a > b > c > d$  (B)  $b > d > c > a$   
(C)  $b > d > a > c$  (D)  $b > c > d > a$

**Sol.**

**Q.8** Rate of the reaction :



is fastest when Z is : **[AIEEE-2004]**

- (A)  $\text{OCOCH}_3$  (B)  $\text{NH}_2$   
(C)  $\text{OC}_2\text{H}_5$  (D)  $\text{Cl}$

**Sol.**

**Q.9** Consider the acidity of the carboxylic acids :  
(1)  $\text{PhCOOH}$  (2)  $o\text{-NO}_2\text{C}_6\text{H}_4\text{COOH}$   
(3)  $p\text{-NO}_2\text{C}_6\text{H}_4\text{COOH}$  (4)  $m\text{-NO}_2\text{C}_6\text{H}_4\text{COOH}$   
Which of the following order is correct ?

**[AIEEE-2004]**

- (A)  $2 > 3 > 4 > 1$  (B)  $2 > 4 > 3 > 1$   
(C)  $2 > 4 > 1 > 3$  (D)  $1 > 2 > 3 > 4$

**Sol.**

**Q.10** On mixing ethyl acetate with aqueous sodium chloride, the composition of the resultant solution is : **[AIEEE-2004]**

- (A)  $\text{CH}_3\text{Cl} + \text{C}_2\text{H}_5\text{COONa}$   
(B)  $\text{CH}_3\text{COONa} + \text{C}_2\text{H}_5\text{OH}$   
(C)  $\text{CH}_3\text{COCl} + \text{C}_2\text{H}_5\text{OH} + \text{NaOH}$   
(D)  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaCl}$

**Sol.**

**Q.11** Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon : **[AIEEE-2004]**

- (A) Butan-2-one (B) Acetic acid  
(C) Acetamide (D) Ethyl acetate

**Sol.**

**Q.12** The compound formed as a result of oxidation of ethyl benzene by  $\text{KMnO}_4$  is -

**[AIEEE-2007]**

- (A) benzophenone (B) acetophenone  
(C) benzoic acid (D) benzyl alcohol

Sol.

**Q.13** A liquid was mixed with ethanol and a drop of concentrated  $\text{H}_2\text{SO}_4$  was added. A compound with a fruity smell was formed. The liquid was : **[AIEEE-2009]**

- (A)  $\text{CH}_3\text{OH}$  (B)  $\text{HCHO}$   
(C)  $\text{CH}_3\text{COCH}_3$  (D)  $\text{CH}_3\text{COOH}$

Sol.

**Q.14** Reaction  
Primary amine +  $\text{CHCl}_3$  +  $\text{KOH} \longrightarrow$  product,  
here product will be - **[AIEEE-2002]**

- (A) Cyanide (B) Isocyanide  
(C) Amine (D) Alcohol

Sol.

**Q.15** The compound formed in the positive test for nitrogen with the Lassaigne solution of an organic compound is - **[AIEEE-2004]**

- (A)  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$   
(B)  $\text{Na}_3[\text{Fe}(\text{CN})_6]$   
(C)  $\text{Fe}(\text{CN})_3$   
(D)  $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]$

Sol.

**Q.16** Which one of the following methods is neither meant for the synthesis nor for separation of amines ? **[AIEEE-2005]**

- (A) Hofmann method (B) Hinsberg method  
(C) Curtius reaction (D) Wurtz reaction

Sol.

**Q.17** Reaction of cyclohexanone with dimethylamine in the presence of catalytic amount of an acid forms a compound if water during the reaction is continuously removed. The compound formed is generally known as - **[AIEEE-2005]**

- (A) an enamine (B) a Schiff's base  
(C) an amine (D) an imine

Sol.

**Q.18** In the chemical reaction,  $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow (\text{A}) + (\text{B}) + 3\text{H}_2\text{O}$ , the compounds (A) and (B) are respectively - **[AIEEE-2007]**

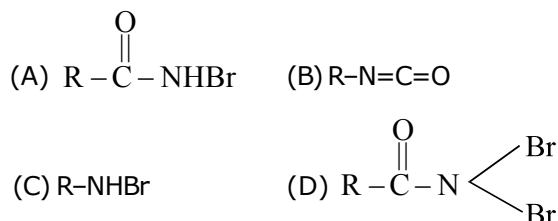
- (A)  $\text{C}_2\text{H}_5\text{CN}$  and  $3\text{KCl}$   
(B)  $\text{CH}_3\text{CH}_2\text{CONH}_2$  and  $3\text{KCl}$   
(C)  $\text{C}_2\text{H}_5\text{NC}$  and  $\text{K}_2\text{CO}_3$   
(D)  $\text{C}_2\text{H}_5\text{NC}$  and  $3\text{KCl}$

Sol.

## LEVEL – II

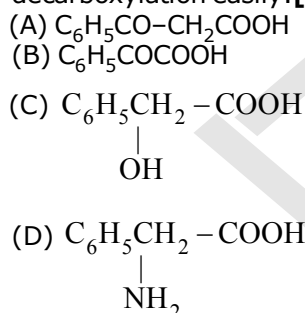
## JEE ADVANCED

- Q.1 The reaction of  $R-\overset{\overset{O}{\parallel}}{C}-NH_2$  with a mixture of  $Br_2$  and  $KOH$  gives  $R-NH_2$  as a product. The intermediates involved in this reaction are: **[IIT 1992]**



Sol.

- Q.2 Which of the following carboxylic acids undergo decarboxylation easily: **[IIT 1995]**



Sol.

- Q.3 The molecular weight of benzoic acid in benzene as determined by depression in freezing point method corresponds to :

**[IIT 1996]**

- (A) Ionization of benzoic acid  
 (B) Dimerisation of benzoic acid  
 (C) Trimerisation of benzoic acid  
 (D) Solvation of benzoic acid

Sol.

- Q.4 When propionic acid is treated with aqueous  $NaHCO_3$ ,  $CO_2$  is liberated. The 'C' of  $CO_2$  comes from **[IIT 1999]**

- (A) Methyl group  
 (B) Carboxylic acid group  
 (C) methylene group  
 (D) bicarbonate

Sol.

- Q.5 Benzoyl chloride is prepared from benzoic acid by:

**[IIT 2000]**

- (A)  $Cl_2, h\nu$       (B)  $SO_2Cl_2$   
 (C)  $SOCl_2$       (D)  $Cl_2, H_2O$

Sol.

- Q.6 Which of the following acids has the smallest dissociation constant? **[IIT 2002]**

- (A)  $CH_3CHFCOOH$       (B)  $FCH_2CH_2COOH$   
 (C)  $BrCH_2CH_2COOH$       (D)  $CH_3CHBrCOOH$

Sol.



Q.7 When benzamide is treated with  $\text{POCl}_3$ , the product is: [IIT 2004]

- (A) Benzonitrile (B) Aniline  
(C) Chlorobenzene (D) Benzylamine

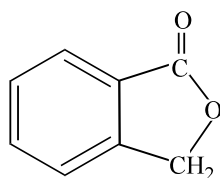
Sol.

Q.8 The correct IUPAC name of  $\text{C}_6\text{H}_5\text{COCl}$  is [IIT 2006]

- (A) Benzoyl chloride  
(B) Benzene chloro ketone  
(C) Benzene carbonyl chloride  
(D) Chloro phenyl ketone

Sol.

Q.9 Which of the following reactants on reaction with conc.  $\text{NaOH}$  followed by acidification gives the following lactone as the only product? [IIT 2006]



- (A) (B)   
(C) (D)

Sol.

Q.10 Match the compounds in **Column I** with their characteristic test(s)/reaction(s) given in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS. [IIT 2008]

**Column I**

- (A)  $\text{H}_2\text{N} - \text{NH}_3^+\text{Cl}^-$   
(B)   
(C)   
(D)

**Column II**

- (P) sodium fusion extract of the compound gives Prussian blue colour with  $\text{FeSO}_4$   
(Q) gives positive  $\text{FeCl}_3$  test  
(R) gives white precipitate with  $\text{AgNO}_3$   
(S) reacts with aldehydes to form the corresponding hydrazone derivative

Sol.

Q.11 Match each of the compound in Column I with its characteristic reaction(s) in Column II.

[IIT 2009]

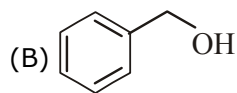
**Column I**

- (A)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$   
 (B)  $\text{CH}_3\text{CH}_2\text{OCOCH}_3$   
 (C)  $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2\text{OH}$   
 (D)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

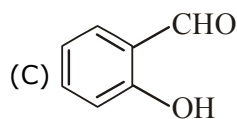
**Column II**

- (P) Reduction with  $\text{Pd-C} / \text{H}_2$   
 (Q) Reduction with  $\text{SnCl}_2 / \text{HCl}$   
 (R) Development of foul smell on treatment with chloroform and alcoholic  $\text{KOH}$   
 (S) Reduction with diisobutylaluminium hydride (DIBAL - H)  
 (T) Alkaline hydrolysis

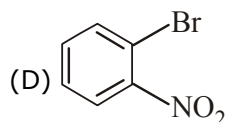
Sol.



(Q) Elimination



(R) Nucleophilic addition



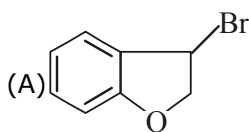
(S) Esterification with acetic anhydride

(T) Dehydrogenation

Sol.

Q.12 Match each of the compounds given in Column I with the reaction(s), that they can undergo, given in Column II. [IIT 2009]

**Column I**

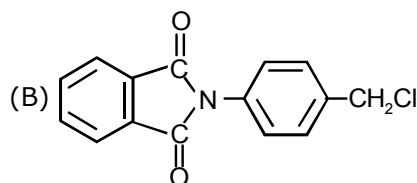
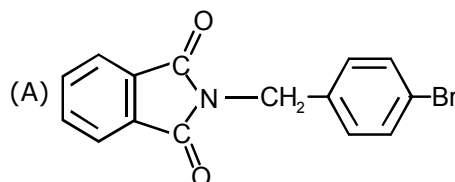
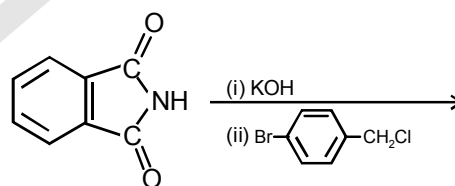


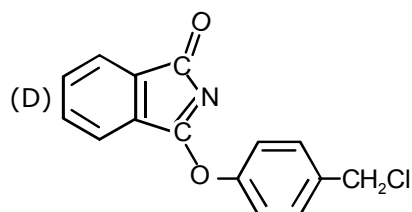
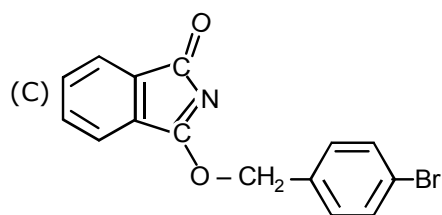
**Column I**

(P) Nucleophilic substitution

Q.13 The major product of the following reaction is

[IIT 2011]





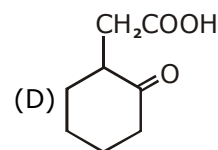
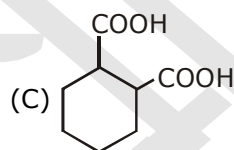
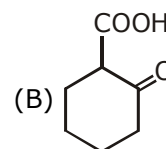
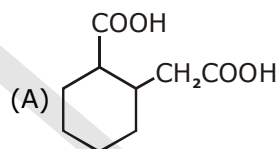
Sol.

Sol.

- Q.14 Among the following compounds, the most acidic is **[IIT 2011]**
- (A) p-nitrophenol  
 (B) p-hydroxybenzoic acid  
 (C) o-hydroxybenzoic acid  
 (D) p-toluic acid

Sol.

- Q.16 The compound that undergoes decarboxylation most readily under mild condition in **[IIT 2012]**



Sol.

- Q.15 The carboxy functional group ( $-\text{COOH}$ ) is present in **[IIT 2012]**
- (A) picric acid  
 (B) barbituric acid  
 (C) ascorbic acid  
 (D) aspirin

# Answers

Answer Ex-I	OBJECTIVE PROBLEMS (JEE MAIN)
-------------	-------------------------------

- |       |       |       |       |       |
|-------|-------|-------|-------|-------|
| 1. C  | 2. C  | 3. C  | 4. B  | 5. C  |
| 6. D  | 7. A  | 8. B  | 9. B  | 10. D |
| 11. A | 12. B | 13. A | 14. B | 15. C |
| 16. B | 17. A | 18. C | 19. D | 20. A |
| 21. D | 22. A | 23. B | 24. A | 25. B |
| 26. D |       |       |       |       |

Answer Ex-II	OBJECTIVE PROBLEMS (JEE ADVANCED)
--------------	-----------------------------------

- |       |       |       |       |       |
|-------|-------|-------|-------|-------|
| 1. A  | 2. B  | 3. C  | 4. A  | 5. D  |
| 6. D  | 7. C  | 8. C  | 9. D  | 10. B |
| 11. C | 12. B | 13. A | 14. B | 15. A |
| 16. A | 17. B | 18. C | 19. D | 20. C |
| 21. C | 22. A | 23. B | 24. B | 25. A |
| 26. D | 27. C | 28. C | 29. A | 30. B |
| 31. A | 32. A | 33. C | 34. A | 35. C |
| 36. B | 37. A | 38. C | 39. A | 40. B |
| 41. B |       |       |       |       |

**Answer Ex-III****SUBJECTIVE PROBLEMS (JEE ADVANCED)**

- |       |       |         |         |        |
|-------|-------|---------|---------|--------|
| 1. A  | 2. B  | 3. A    | 4. A    | 5. D   |
| 6. C  | 7. C  | 8. C    | 9. B    | 10. B  |
| 11. C | 12. C | 13. B   | 14. C   | 15. D  |
| 16. D | 17. A | 18. D   | 19. C   | 20. B  |
| 21. C | 22. B | 23. B,D | 24. ACD | 25. BD |

**Answer Ex-IV****PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

- |       |       |       |       |       |
|-------|-------|-------|-------|-------|
| 1. C  | 2. C  | 3. A  | 4. D  | 5. D  |
| 6. C  | 7. D  | 8. D  | 9. A  | 10. D |
| 11. A | 12. C | 13. D | 14. B | 15. A |
| 16. D | 17. A | 18. A |       |       |

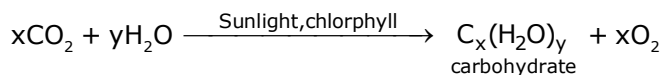
**LEVEL – II****JEE ADVANCED**

- |  |                                       |       |       |      |
|--|---------------------------------------|-------|-------|------|
| 1. A,B                                   | 2. A                                  | 3. B  | 4. D  | 5. C |
| 6. C                                     | 7. A                                  | 8. C  | 9. C  |      |
| 10. (A) R,S ;(B) P,Q; (C) P,Q,R ;(D) P,S |                                       |       |       |      |
| 11. (A) P,Q,S,T (B) P,S,T (C) P (D) R    | 12. (A) P,Q,T (B) P,S,T (C) R,S (D) P |       |       |      |
| 13. A                                    | 14. C                                 | 15. D | 16. B |      |

## CARBOHYDRATES

### 1. Introduction:

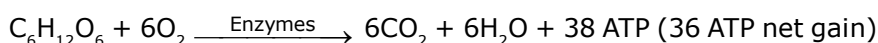
Carbohydrates received their name because of their general formula  $C_x(H_2O)_y$ , according to which they appear to be hydrates of carbon.



#### Photosynthesis



#### Cellular Respiration



### 2. Classification and structure of Carbohydrates:

Carbohydrates are polyhydroxy aldehydes and ketones and substances which hydrolyse to polyhydroxy aldehydes and ketones.

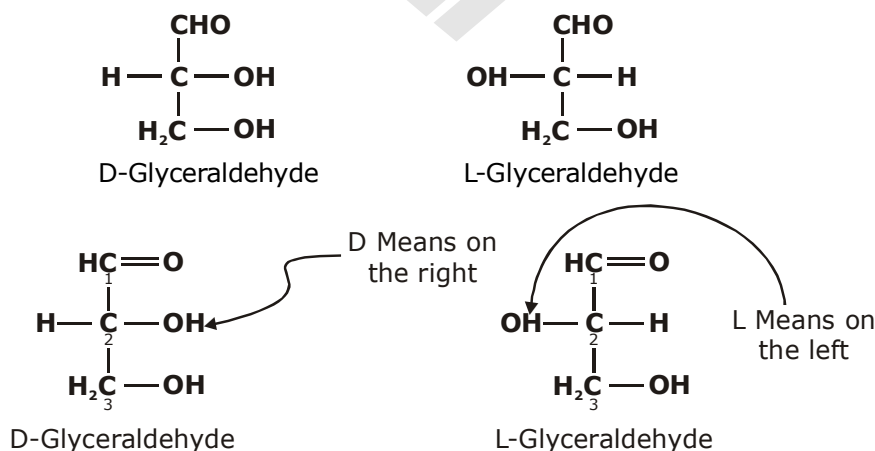
The simplest carbohydrates are called **sugars** or **saccharides**, (Latin: Saccharum, sugar). Carbohydrates can be classified as **monosaccharides**, **oligosaccharides** and **polysaccharides**.

### 3. General Characteristic of Monosaccharides:

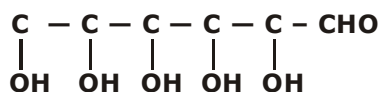
The important characteristics of monosaccharides are as follows:

- (i) All monosaccharides are water soluble due to the presence of hydrogen bonding between the different OH groups and surrounding water molecules.
- (ii) Monosaccharides have sweet taste and upon heating they get charred and give the smell of burning sugar.
- (iii) Monosaccharides are optically active in nature due to the presence of chiral carbon atoms.
- (iv) The chemical characteristics of monosaccharides are due to OH groups and carbonyl group which may be either aldehydic or ketonic group.

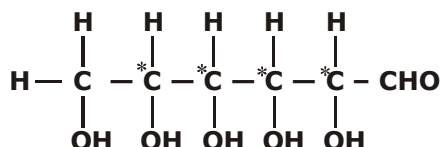
Glyceraldehyde contains one asymmetric carbon atom (marked by an asterisk) and can thus exist in two optically active forms, called the D-form and the L-form. Clearly, the two forms are mirror images that cannot be superimposed, that is they are **enantiomers**.



All four isomers have been prepared synthetically. The D- and L-erythrose are mirror images, that is, they are enantiomers. They have exactly the same degree of rotation but in opposite directions. Equal amounts of the two would constitute a racemic mixture, that is a mixture that would allow a plane-polarised light to pass through the solution unchanged.



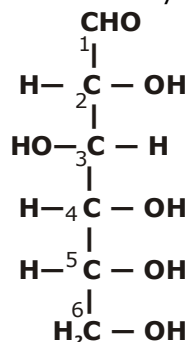
Supplying hydrogen atoms to the five carbon atoms to satisfy their tetravalency, following structure (open chain) may be assigned to glucose: (\* indicates assymetric carbon atom).



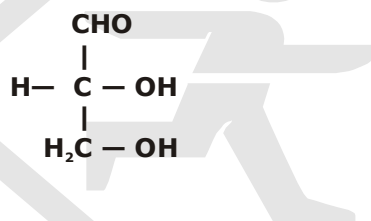
## 6. Configuration\* of Glucose:

Since the above structure possesses four asymmetric carbon atoms (shown by asterisks), it can exist in  $2^4 = 16$  optically active forms, i.e., eight pairs of enantiomers. All these are known and correspond to the D- and L-forms of glucose, mannose, galactose, allose, glucose, idose and talose.

The naturally occurring dextrorotatory glucose (+)-glucose is only one of the 16-stereoisomers.



D(+)-Glucose



(+)-Glyceraldehyde

Notations D- and L- for denoting configuration were given by Rosanof; according to this convention any compound whose bottom asymmetric carbon atom has the configuration similar to the configuration of dextrorotatory glyceraldehyde (drawn above, i.e. the bottom carbon atom has -OH to the left and H to the right) is given L-configuration. Remember that the symbols D- and L- have no relation with the specific rotation value, i.e., with (+) or (-) value. For example, the natural (-) fructose belongs to D-series, i.e., it is D(-)-fructose.

## 7. Objections to open-chain structure of glucose:

Even though open chain structure of (+) glucose explains most of its reactions, it fails to explain the following facts about it.

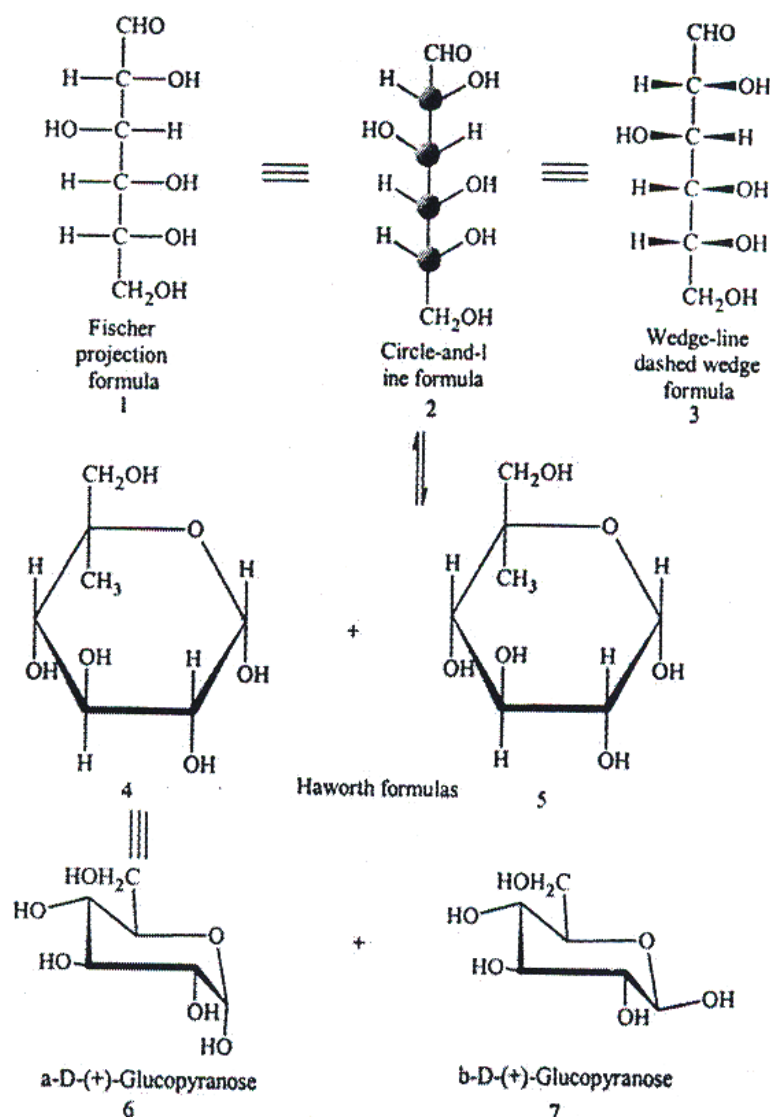
- Glucose does not restore Schiff's reagent colour.
- Glucose does not form a bisulphite and aldehyde-ammonia compound.
- Glucose forms two isomeric penta-acetates neither of which reacts with carbonyl reagents.
- The existence of the two isomeric glucoses and the change in specific rotation (mutarotation) is not explained by an open-chain formula.
- Glucose reacts with methanol in presence of dry HCl gas to form two isomeric glucosides. Since glucose is less soluble in ethanol, it separates out on cooling the reaction mixture. Commercially, it is obtained by the hydrolysis of starch which is available from relatively inexpensive source such as maize, potatoes and rice.





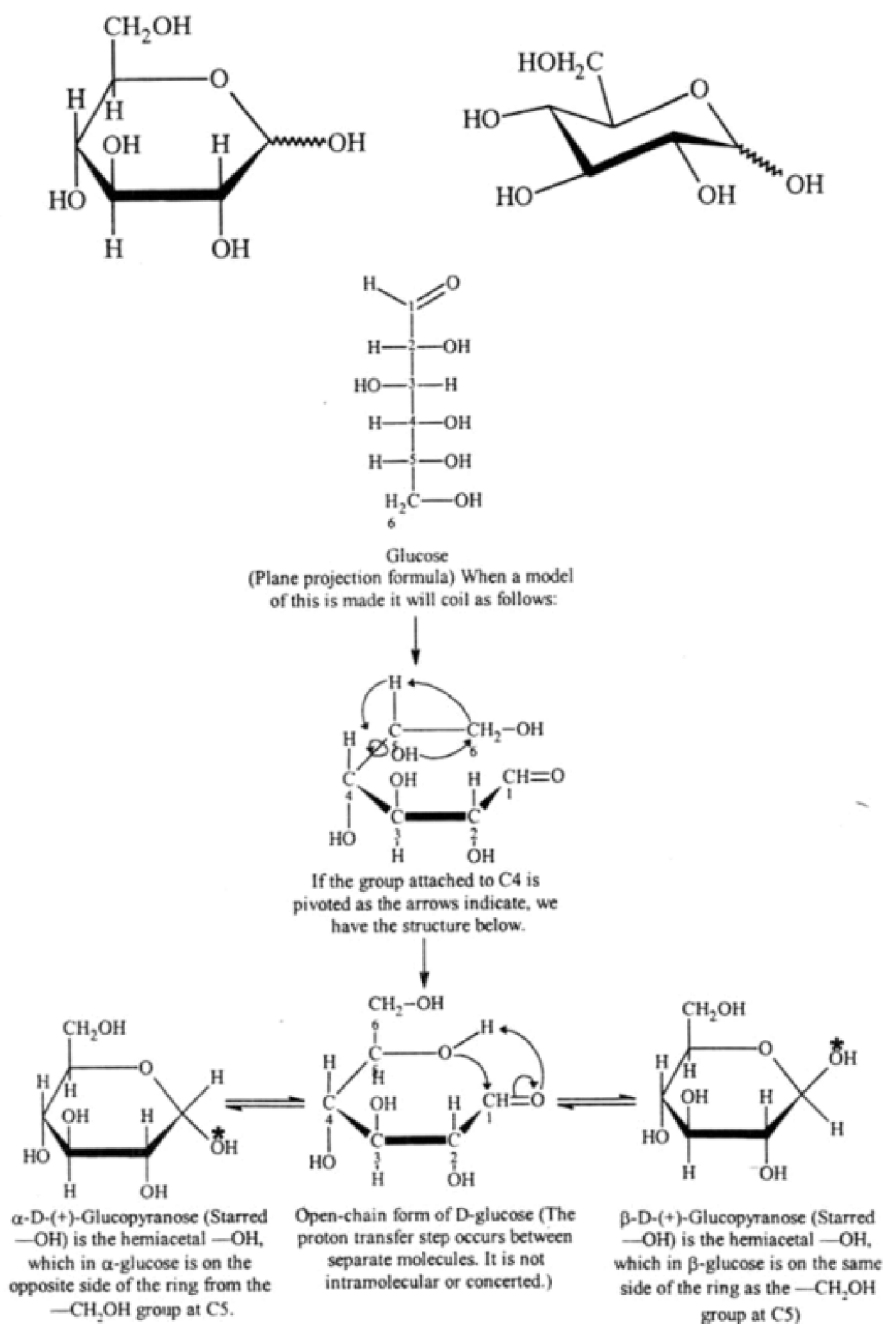
**STRUCTURE FORMULAS FOR MONOSACCHARIDES:**

Although many of the properties of D(+)-glucose can be explained in terms of an open-chain structure (1, 2, or 3), a considerable body of evidence indicates that the open-chain structure exists, primarily, in equilibrium with two cyclic forms. These can be represented by structures 4 and 5 or 6 and 7. The cyclic forms of D(+)-glucose are hemiacetals formed by an intramolecular reaction of the -OH group at C5 with the aldehyde group. Cyclization creates a new stereogenic centre at C1, and this stereogenic centre explains how two cyclic forms are possible. These two cyclic forms are diastereomers that differ only in the configuration of C1. In carbohydrate chemistry diastereomers of this type are called anomers, and the hemiacetal carbon atom is called the anomeric carbon atom.



Structures 4 and 5 for the glucose anomers are called Haworth formulas and, although they do not give an accurate picture of the shape of the six-membered ring, they have many practical uses. Demonstrates how the representation of each stereogenic centre of the open-chain form can be correlated with its representation in the Haworth formula.

Each glucose anomer is designated as an  $\alpha$  anomer or a  $\beta$  anomer depending on the location of the -OH group of C1. When we draw the cyclic forms of a D sugar in the

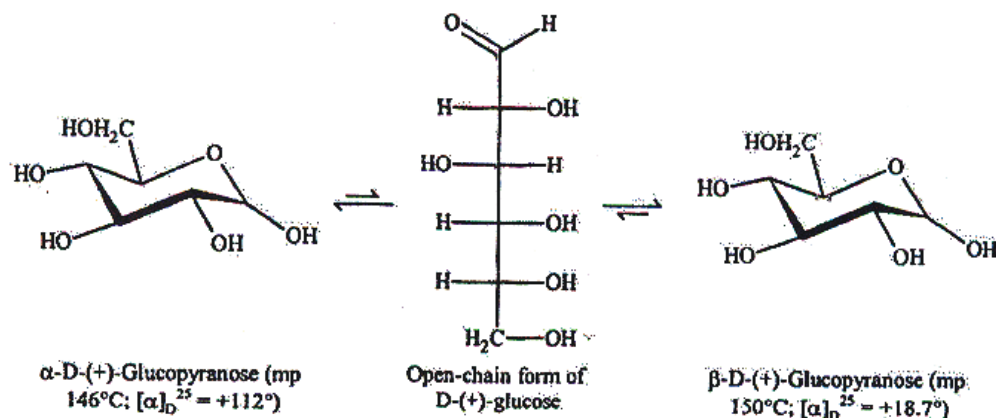


### MUTAROTATION:

Ordinary D(+)-glucose has a melting point of 146°C. However, when D(+)-glucose is crystallized by evaporating an aqueous solution kept above 98°C, a second form of D(+)-glucose with a melting point of 150°C can be obtained. When the optical rotations of these two forms are measured, they are found to be significantly different, but when an aqueous solution of either form is allowed to stand, its rotation changes. The specific rotation of one form decreases and the rotation of the other increases, until both solutions

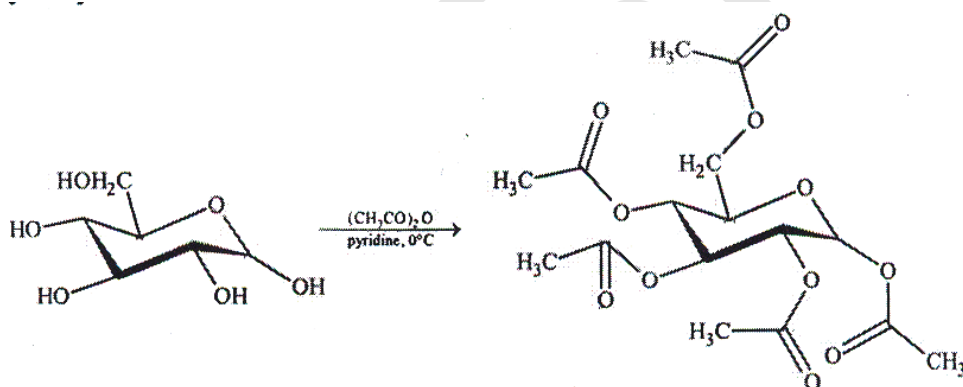
show the same value. A solution of original D-(+)-glucose (mp 146°C) has an initial specific rotation of +112°, but, ultimately, the specific rotation of this solution falls to +52.7°. A solution of second form of D(+) glucose (mp 150°C) has an initial specific rotation of +18.7°, but slowly, the specific rotation of this solution rises to +52.7°. This change in rotation towards an equilibrium value is called mutarotation.

The explanation for this mutarotation lies in the existence of an equilibrium between the open-chain form of D-(+) glucose and the  $\alpha$  and  $\beta$  forms of the cyclic hemiacetals.



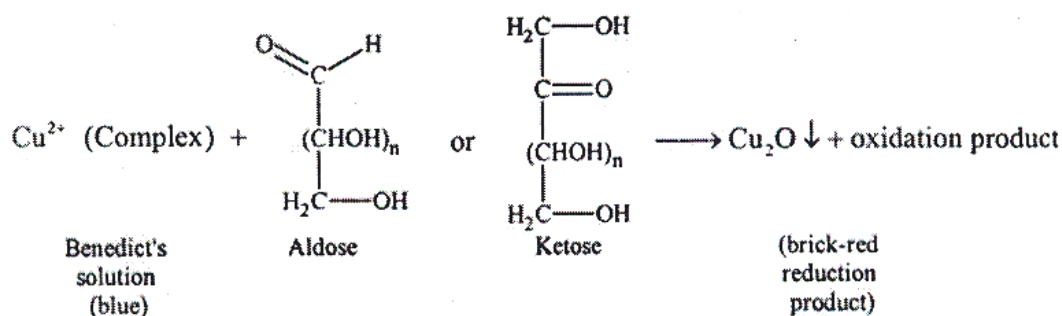
### CONVERSION TO ESTERS:

Treating a monosaccharide with excess acetic anhydride and a weak base (such as pyridine or sodium acetate) converts all of the hydroxyl groups, including the anomeric hydroxyl, to ester groups. If the reaction is carried out at a low temperature (e.g.,  $0^\circ\text{C}$ ), the reaction occurs stereospecifically; the  $\alpha$  anomer gives the  $\alpha$ -acetate and the  $\beta$  anomer gives the  $\beta$ -acetate. Acetate esters are common protecting groups for carbohydrate hydroxyls.



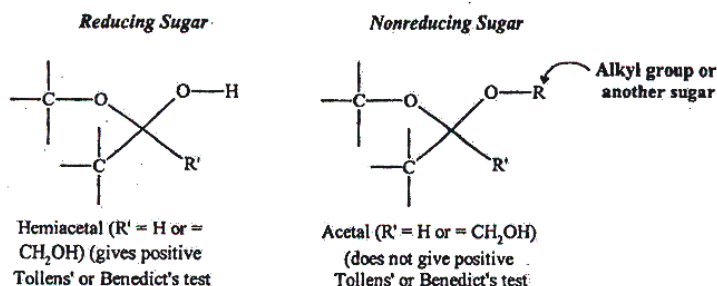
### BENEDICT'S OR TOLLENS' REAGENTS: REDUCING SUGARS

Benedict's reagent (A alkaline solution containing a cupric citrate complex ion) and Tollen's solution  $[\text{Ag}^+(\text{NH}_3)_2\text{OH}]^-$  oxidize and thus give positive tests with aldoses and ketoses. The tests are positive even though aldoses and ketoses exist primarily as cyclic hemiacetals.



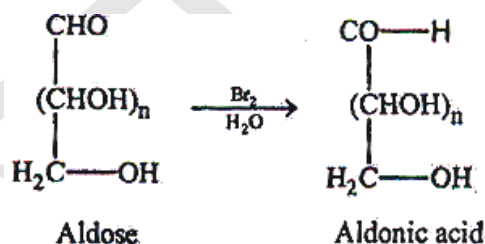
Sugars that give positive tests with Tollen's or Benedict's solutions are known as reducing sugars, and all carbohydrates that contain a hemiacetal group given positive tests. In aqueous solution these hemiacetals exist in equilibrium with relatively small, but not insignificant, concentrations of noncyclic aldehydes or  $\alpha$ -hydroxy ketones. It is the latter two that undergoes the oxidation until one reactant is exhausted.

Carbohydrates that contain only acetal groups do not give positive tests with Benedict's or Tollen's solutions, and they are called non-reducing sugars. Acetals do not exist in equilibrium with aldehydes or  $\alpha$ -hydroxy ketones in the basic aqueous media of the test reagents.

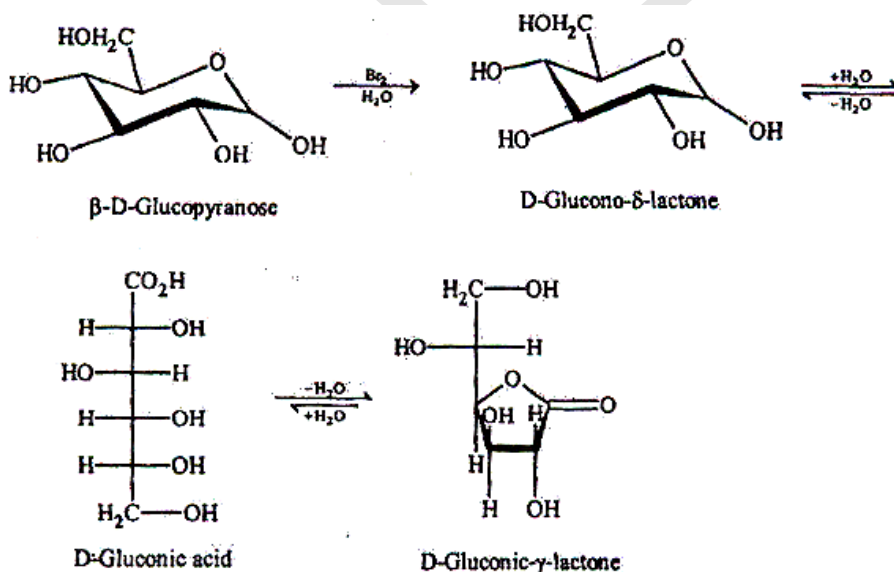


### BROMINE WATER : THE SYNTHESIS OF ALDONIC ACID

Monosaccharides do not undergo isomerization and fragmentation reactions in mildly acidic solution. Thus, a useful oxidizing reagent for preparative purposes is bromine in water (pH 6.0). Bromine water is a general reagent that selectively oxidizes the  $-CHO$  group to a  $-CO_2H$  group. It converts an aldose to an aldonic acid.

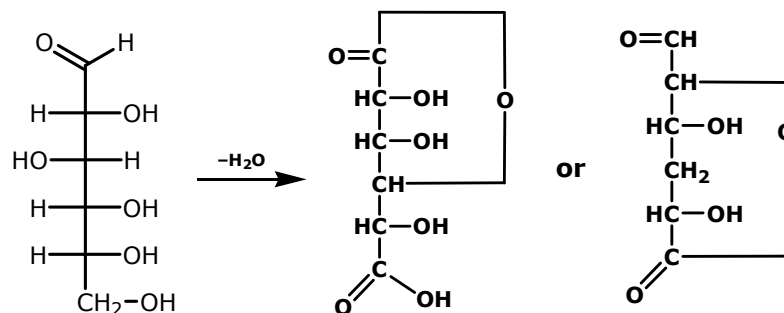


Experiments with aldopyranoses have shown that the actual course of the reaction is somewhat more complex than we have indicated above. Bromine water specifically oxidizes the  $\beta$  anomer, and the initial product that forms is a  $\delta$ -aldonolactone. This compound may then hydrolyze to an aldonic acid, and the aldonic acid may undergo a subsequent ring closure to form a  $\gamma$ -aldonolactone:



**NITRIC ACID OXIDATION: ALDARIC ACID**

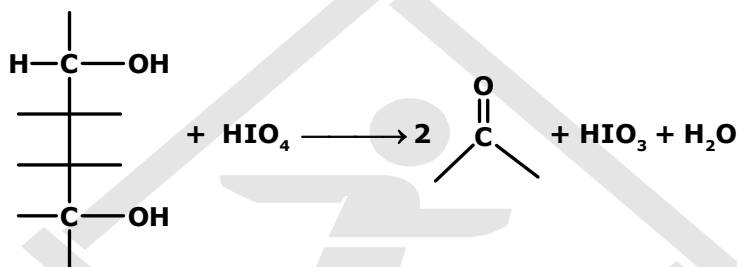
Dilute nitric acid – a stronger oxidizing agent than bromine water – oxidizes the both  $-CHO$  group and the terminal  $-CH_2OH$  group of an aldose to  $-CO_2H$  groups. These dicarboxylic acids are known as aldaric acids:



This aldaric acid obtained from D-glucose is called D-glucoaric acid.

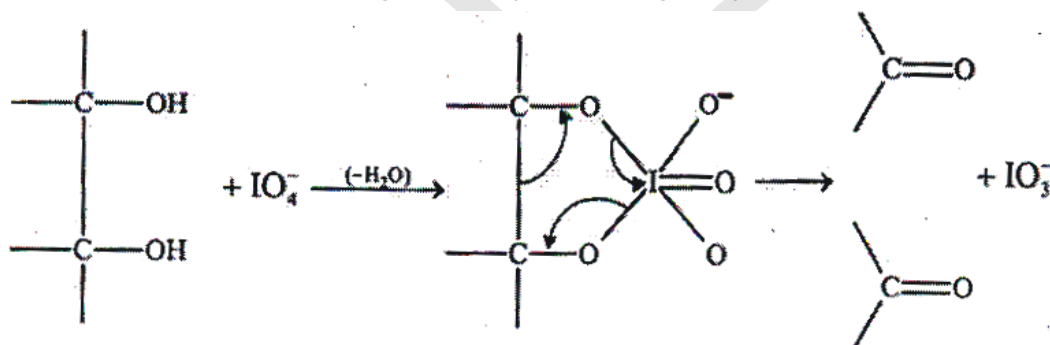
**PERIODATE OXIDATION: OXIDATIVE CLEAVAGE OF POLYHYDROXY COMPOUNDS**

Compounds that have hydroxyl groups on adjacent atoms undergo oxidative cleavage when they are treated with aqueous periodic acid ( $HIO_4$ ). The reaction breaks carbon-carbon bonds and produces carbonyl compounds (aldehydes, ketones, or acids).



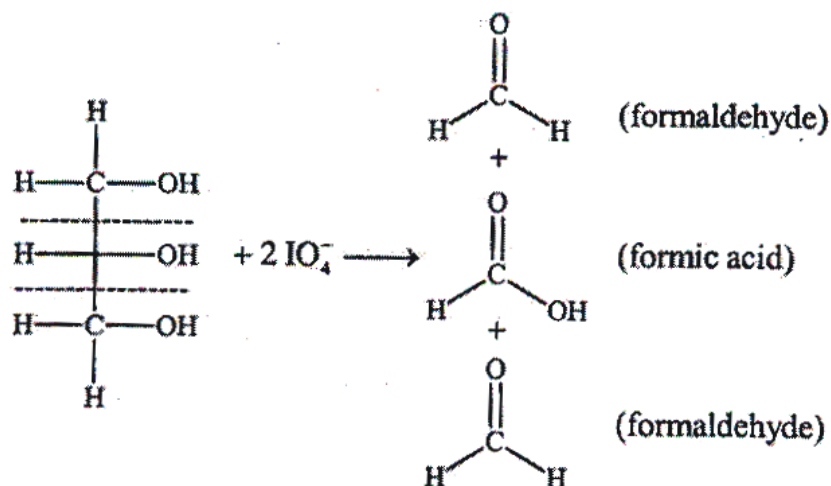
Since the reaction usually takes place in quantitative yield, valuable information can often be gained by measuring the number of molar equivalents of periodic acid that is consumed in the reaction as well as by identifying the carbonyl products.

Periodate oxidations are thought to take place through a cyclic intermediate:

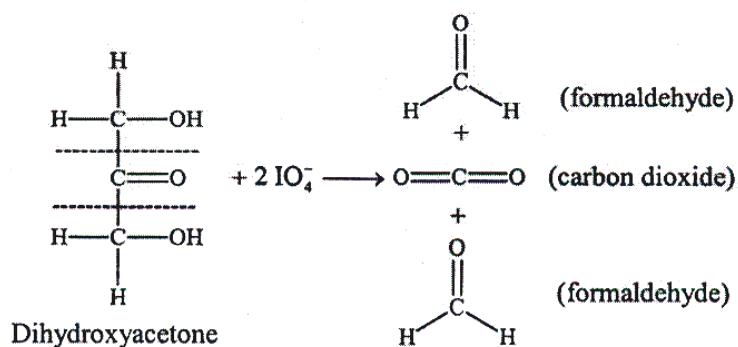
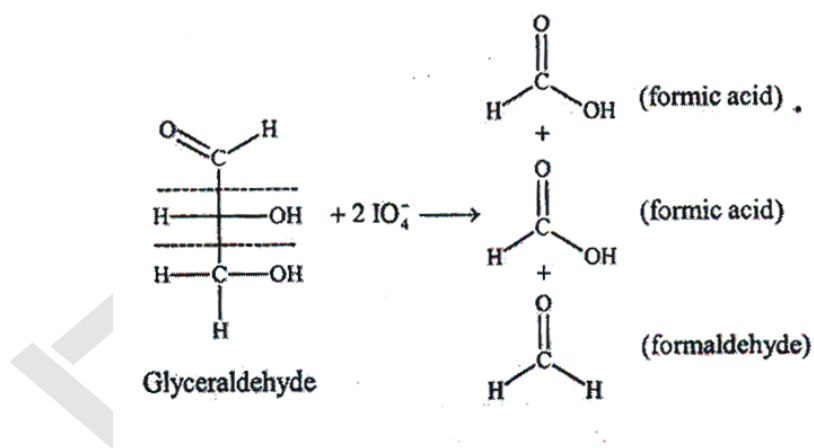


Before we discuss the use of periodic acid in carbohydrate chemistry, we should illustrate the course of the reaction with several simple examples. Notice in these periodate oxidations that for every C - C bond broken, a C - O bond is formed at each carbon.

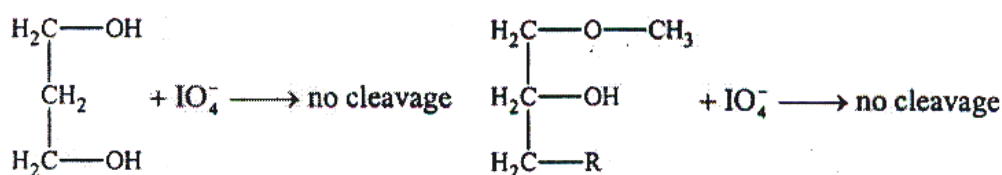
1. When three or more  $-CHOH$  groups are continuous, the internal ones are obtained as formic acid. Periodate oxidation of glycerol, for example, gives two molar equivalents of formaldehyde and one molar equivalent of formic acid;



2. Oxidative cleavage also takes place when an -OH group is adjacent to the carbonyl group of an aldehyde or ketone (but not that of an acid or an ester). Glyceraldehyde yields two molar equivalents of formic acid and one molar equivalent of formaldehyde, while dihydroxyacetone gives two molar equivalents of formaldehyde and one molar equivalent of carbon dioxide.

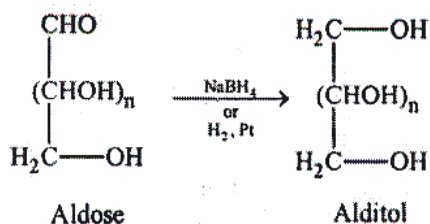


Periodic acid does not cleave compounds in which the hydroxyl groups are separated by an intervening -CH<sub>2</sub> group, nor those in which a hydroxyl group is adjacent to an ether or acetal.



**REDUCTION OF MONOSACCHARIDES: ALDITOLS**

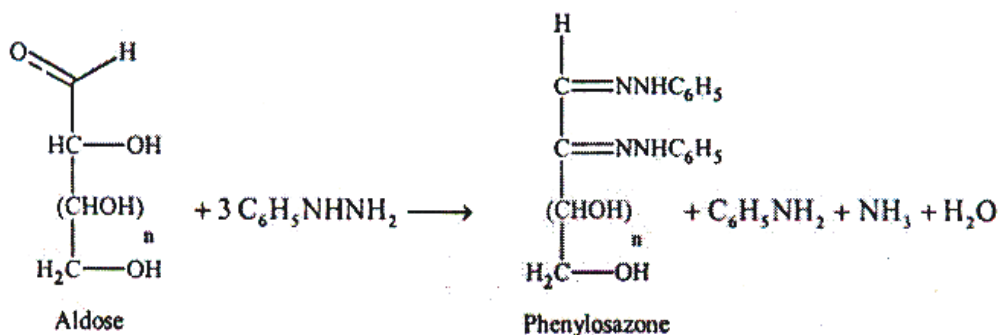
Aldoses (and ketoses) can be reduced with sodium borohydride to compounds called alditols:



Reduction of D-glucose, for example, yields D-glucitol.

**REACTIONS OF MONOSACCHARIDES WITH PHENYLHYDRAZINE: OSAZONES**

The aldehyde group of an aldose reacts with such carbonyl reagents as hydroxylamine and phenylhydrazine. With hydroxylamine, the product is the expected oxime. With enough phenylhydrazine, however, three molar equivalents of phenylhydrazine are consumed and a second phenylhydrazone group is introduced at C2. The product is called a phenylosazone. Phenylosazones crystallize readily (unlike sugars) and are useful derivatives for identifying sugars.

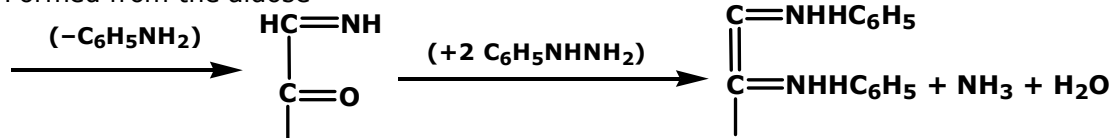


The mechanism for osazone formation probably depends on a series of reaction in which

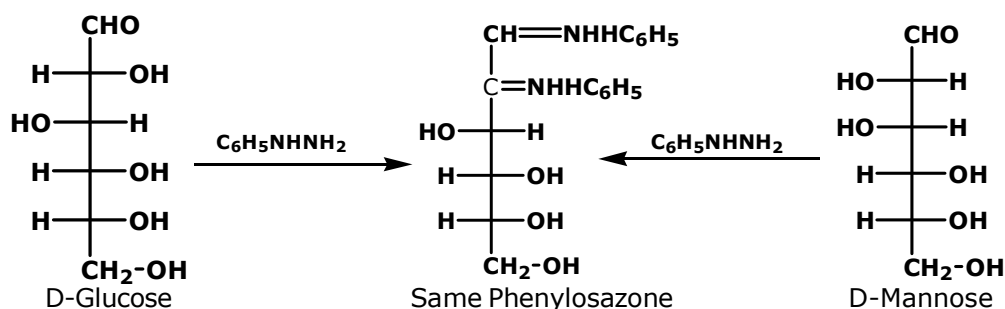
behaves very much like  $\text{C}=\text{O}$  in giving a nitrogen version of an enol.

**A Mechanism for the Reaction  
Phenylosazone Formation**

Formed from the aldose



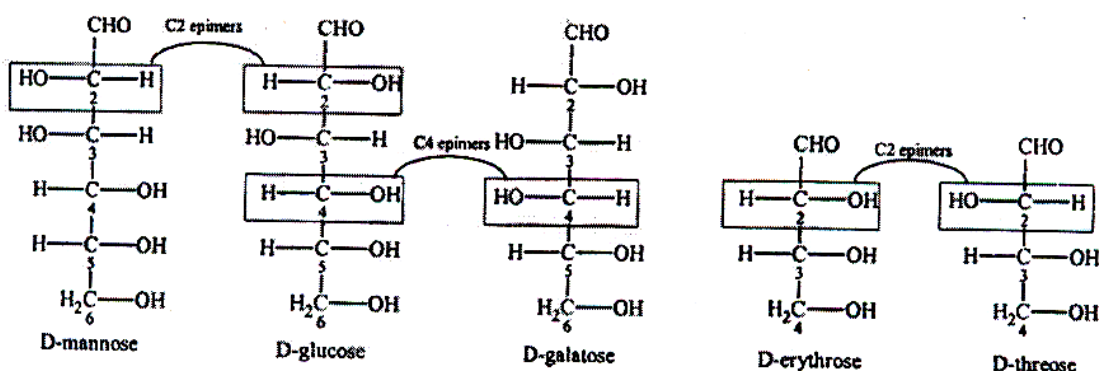
Osazone formation results in a loss of the stereogenic centre at C2 but does not affect other stereogenic carbons; D-glucose and D-mannose, for example, yield the same phenylosazone:



This experiment, first done by Emil Fischer, established that D-glucose and D-mannose have the same configuration about C3, C4 and C5. Diastereomeric aldoses that differ in configuration at only one carbon (such as D-glucose and D-mannose) are called epimers. In general, any pair of diastereomers that differ in configuration at only a single tetrahedral stereogenic carbon can be called epimers.

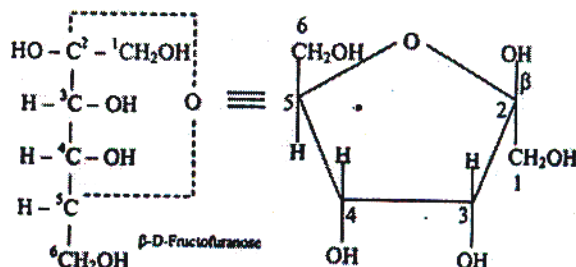
### Epimers:

Many common sugars are closely related, differing only by the stereochemistry at a single carbon atom. For example, glucose and mannose differ only at C2, the first asymmetric carbon atom. Sugars that differ only by the stereochemistry at a single carbon are called **epimers**, and the carbon atom where they differ is generally stated. If the number of a carbon atom is not specified, it is assumed to be C2. Therefore, glucose and mannose are "C2 epimers" or simply "epimers". The C4 epimer of glucose is galactose and the C2 epimer of erythrose is threose.



### Cyclic structure of Fructose:

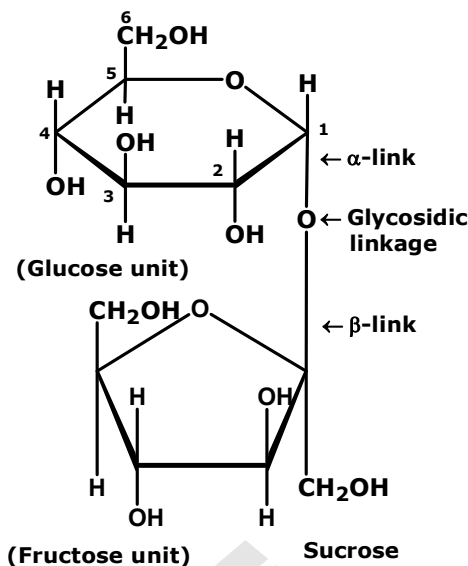
Like glucose, fructose also has a cyclic structure. Since fructose contains a keto group, it forms an intramolecular hemiketal. In the hemiketal formation, C5-OH of the fructose combines with C2-keto group. As a result, C2 becomes chiral and thus has two possible arrangements of CH<sub>2</sub>OH and OH group around it. Thus,



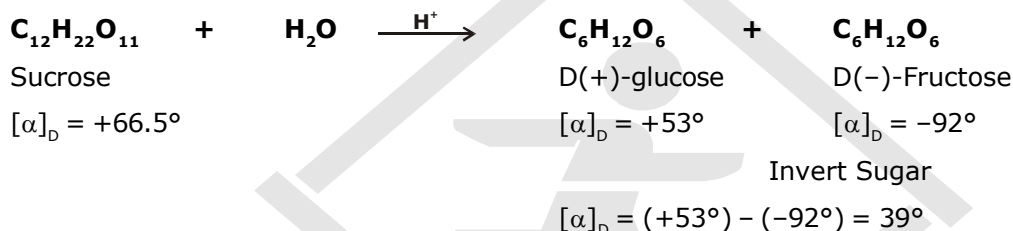


D-fructose exists in two stereoisomeric forms, i.e.,  $\alpha$ -fructopyranose and  $\beta$ -D fructopyranose. However in the combined state (such as sucrose), fructose exists in furanose form as shown below:

### Hydrolysis of Sucrose:



(Invert Sugar or Invertose). Hydrolysis of sucrose with hot dilute acid yields D-glucose and D-fructose.



Sucrose is dextrorotatory, its specific rotation being  $+66.5^\circ$ , D-glucose is also dextrorotatory,  $[\alpha]_D = +53^\circ$ , but D-fructose has a large negative rotation,  $[\alpha]_D = -92^\circ$ . Since D-fructose has a greater specific rotation than D-glucose, the resulting mixture is laevorotatory. Because of this the hydrolysis of sucrose is known as the inversion of sucrose, and the equimolecular mixture of glucose and fructose is known as invert sugar or invertose.

## POLYSACCHARIDES

Polysaccharides are the polymers of monosaccharides. The natural polysaccharides generally contain about 100-3000 monosaccharide units. The three most abundant natural polysaccharides-cellulose, starch and glycogen are derived from the same monomer, i.e., glucose.

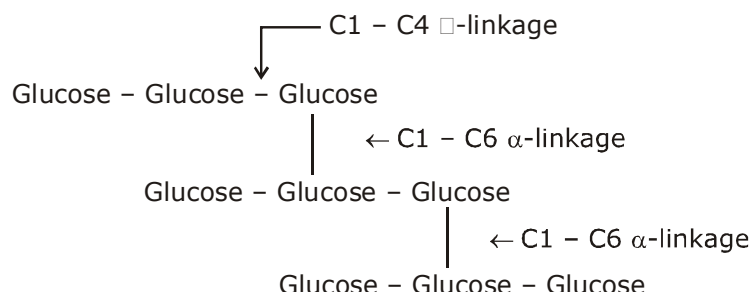
**Starch:** It is a polymer of glucose. Its molecular formula is  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$  where the value of  $n$  (200 – 1000) varies from source to source. It is the chief food reserve material or storage polysaccharide of plants and is found mainly in seeds, roots, tubers, etc. Wheat, rice, potatoes, corn, bananas etc., are rich source of starch.

Starch is not a single compound but is a mixture of two components – a water soluble component called amylose (20%) and a water insoluble component called amylopectin (80%). Both amylose and amylopectin are polymers of  $\alpha$ -D glucose.

Amylose is a linear polymer of  $\alpha$ -D glucose. It contains about 200 glucose units which are linked to one another through  $\alpha$ -linkage involving  $\text{C}_1$  of one glucose unit with  $\text{C}_4$  of the other.

Amylopectin, on the other hand, is a highly branched polymer. It consists of a large number (several branches) of short chains each containing 20-25 glucose units which are joined together through  $\alpha$ -linkages involving C1 of one glucose unit with C4 of the other. The C1 of terminal glucose unit in each chain is further linked to C6 of the other glucose.

unit in the next chain through C1-C6  $\alpha$ -linkage. This gives amylopectin a highly branched structure as shown below:



### Hydrolysis:

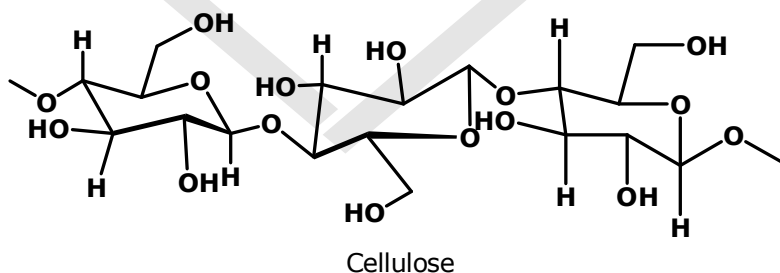
Hydrolysis of starch with hot dilute acids or by enzymes give dextrins of varying complexity, maltose and finally D-glucose. Starch does not reduce Tollen's reagent and Fehling's solution.

### Uses:

It is used as a food. It is encountered daily in the form of potatoes, bread, cakes, rice etc. It is used in coating and sizing paper to improve the writing qualities. Starch is used to treat textile fibres before they are woven into cloth so that they can be woven without breaking. It is used in manufacture of dextrins, glucose and ethyl alcohol. Starch is also used in manufacture of starch nitrate, which is used as an explosive.

### Cellulose:

Cellulose is the chief component of wood and plant fibres; cotton, for instance, is nearly pure cellulose. It is insoluble in water and tasteless; it is a non-reducing carbohydrate. These properties, in part at least, are due to extremely high molecular weight.



Cellulose has the formula  $(C_6H_{10}O_5)_n$ . Complete hydrolysis by acid yields D(+)-glucose as the monosaccharide. Hydrolysis of completely methylated cellulose gives a high yield of 2, 3, 6-tri-O-methyl-D-glucose. Like starch, therefore, cellulose is made up of chains of D-glucose units, each unit joined by a glycoside linkage of C-4 of the next.

Cellulose differs from starch, however, in the configuration of the glycoside linkage. Upon treatment with acetic anhydride and sulfuric acid, cellulose yields octa-O-acetylcellobiose, there is evidence that all glycoside linkages in cellulose, like the one in (+) cellobiose, are *beta* linkages.

Physical methods give molecular weights for cellulose ranging from 250000 to 1000000 or more; it seems likely that there are at least 1500 glucose units per molecule. End group analysis by both methylation and periodic acid oxidation gives a chain length of 1000 glucose units or more. X-ray analysis and electron microscopy indicate that these long chains lie side by side in bundles, undoubtedly held together by hydrogen bonds between the numerous neighbouring –OH groups. These bundles are twisted together to form.

Rope like structure which themselves are grouped to form the fibers we can see. In wood these cellulose “ropes” are embedded in lignin to give a structure that has been likened to reinforced concrete.

### **Properties of Cellulose:**

We have seen that the glycoside linkages of cellulose are broken by the action of acid, each cellulose molecule yielding many molecules of D(+)-glucose. Now let us look briefly at reactions of cellulose in which the chain remains essentially intact. Each glucose unit in cellulose contains three free –OH groups; these are the positions at which reactions occur.

These reactions of cellulose, carried out to modify the properties of a cheap, available ready-made polymer, are of tremendous industrial importance.

Like any alcohol, cellulose forms **esters**. Treatment with a mixture of nitric and sulfuric acid converts cellulose into *cellulose nitrate*. The properties and uses of the product depend upon the extent of nitration. *Guncotton*, which is used in making smokeless powder, is very nearly completely nitrated cellulose, and is often called cellulose trinitrate (three nitrate groups per glucose unit). *Pyroxylin* is less highly nitrated material containing between two and three nitrate groups per glucose unit. It is used in the manufacture of plastics like celluloid and collodion, in photographic film, and in lacquers. It has the disadvantage of being flammable, and forms highly toxic nitrogen oxides upon burning.

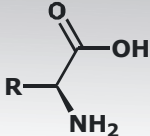
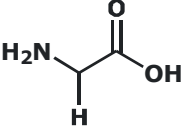
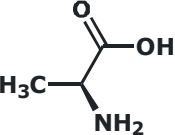
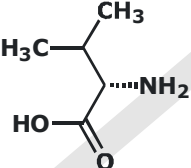
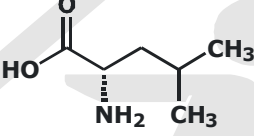
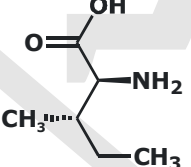
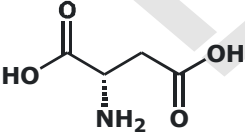
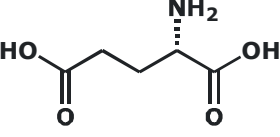
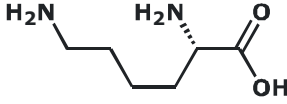
Industrially, cellulose is alkylated to **ethers** by the action of alkyl chlorides (cheaper than sulfates) in the presence of alkali. Considerable degradation of the long chain is unavoidable in these reactions. Methyl, ethyl, and benzyl ethers of cellulose are important in the production of textiles, films, and various plastic objects.

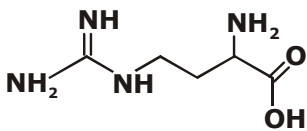
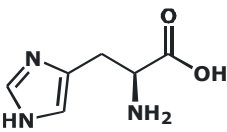
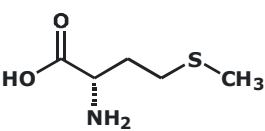
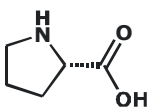
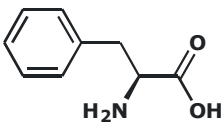
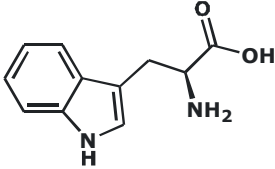
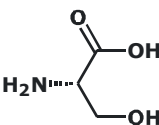
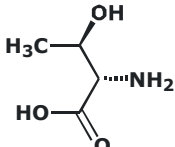
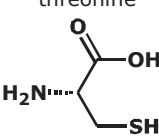
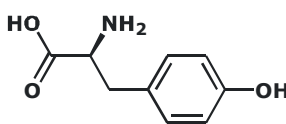
## **AMINO ACIDS**

### **1. Introduction:**

Amino acids are the compounds which contain both an amino group and a carboxy group in their molecules. They constitute a particularly important class of difunctional compounds as they are the building blocks of proteins.

While several hundred different amino acids are known to occur naturally, 20 of them deserve special mention as they are present in proteins. These amino acids are listed in Table. As given in this table, for amino acids trivial names are common. The convention to use a three letter code, as an abbreviation, for each amino acid is also given in the table. These abbreviations are particularly useful in designating the sequence of amino acids in peptides and proteins which you will study.

Nature of amino acid	E/N.E		Name	Abbreviation
Neutral amino acid	NE		Glycine	Gly
Neutral amino acid	NE		Alanine	Ala
Neutral amino acid	E		Valine	Val
Neutral amino acid	E		Leucine	Leu
Neutral amino acid	E		Isoleucine	Ile
Acidic amino acid	NE		Aspartic Acid	Asp
Acidic amino acid	NE		Glutamic Acid	Glu
Basic amino acid	E		Lysine	Lys

Basic amino acid	NE		Arginin	Arg
Basic amino acid	NE		Histidine	His
Neutral amino acid	E		Methionine	Met
Neutral amino acid	NE		Proline	Pro
Neutral amino acid	E		Phenylalanine	Phe
Neutral amino acid	E		Tryptophan	Trp
Neutral amino acid	NE		Serine	Ser
Neutral amino acid	E		Threonine	Thr
Neutral amino acid	NE	threonine 	Cysteine	Cys
Neutral amino acid	NE		Tyrosine	Tyr

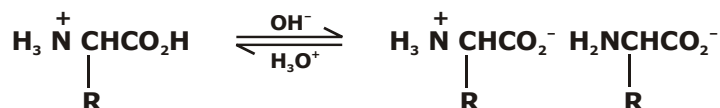
E = essential amino acid

NE = Non essential amino acid

**AMINO ACID AS DIPOLAR IONS:**

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Amino Acids contain both a basic group ( $-\text{NH}_2$ ) and an acidic group ( $-\text{COOH}$ ). In the dry solid state, amino acids exist as dipolar ions, a form in which the carboxyl group is present as a carboxylate ion,  $-\text{CO}_2^-$ , and the amino group is present as an aminium ion,  $-\text{NH}_3^+$  (Dipolar ions are also called zwitterions.) In aqueous solution, an equilibrium exists between the dipolar ion and the anionic and cationic forms of an amino acids.

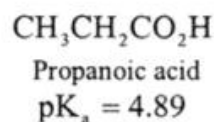
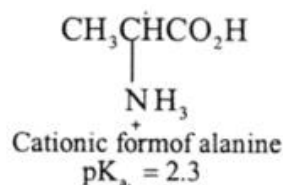


Cationic form (Predominant in strongly acidic solutions, e.g., At pH 0)

Dipolar ion

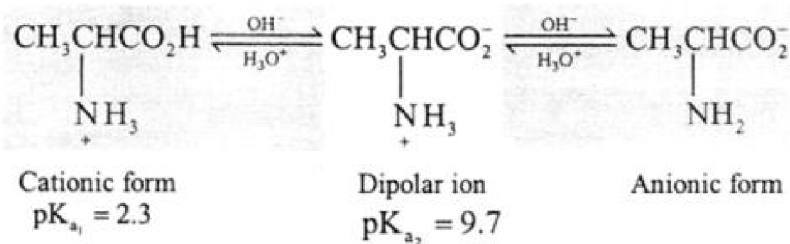
Anionic form (Predominant in strongly basic solutions, e.g., At pH 14)

If alanine is dissolved in a strongly acidic solution (e.g. pH 0), it is present in mainly a net cationic form. In this state the amine group is protonated (bears a formal +1 charge) and the carboxylic acid group is neutral (has no formal charge). As is typical of  $\alpha$ -amino acids, the  $\text{pK}_a$  for the carboxylic acid hydrogen of alanine is considerably lower (2.3) than the  $\text{pK}_a$  of an ordinary carboxylic acid (e.g., propanoic acid,  $\text{pK}_a$  4.89):



The reason for this enhanced acidity of the carboxyl group in an  $\alpha$ -amino acid is the inductive effect of the neighboring aminium cation, which helps to stabilize the carboxylate anion formed when it loses a proton. Loss of proton from the carboxyl group in a cationic  $\alpha$ -amino acid leaves the molecule electrically neutral (in the form of a dipolar ion). This equilibrium is shown in the red-shaded portion of the equation below.

The protonated amine group of an  $\alpha$ -amino acid is also acidic, but less so than the carboxylic acid group. The  $\text{pK}_a$  of the aminium group in alanine is 9.7. The equilibrium for loss of an aminium proton is shown in the blue-shaded portion of the equation below. The carboxylic acid proton is always lost before a proton from the aminium group in an  $\alpha$ -amino acid.



The state of an  $\alpha$ -amino acid at any given pH is governed by a combination of two equilibria, as shown in the above equation for alanine. The isoelectric point (pI) of an amino acid such as alanine is the average of  $\text{pK}_{a1}$  and  $\text{pK}_{a2}$ ;

$$\text{pI} = \frac{1}{2} (2.3 + 9.7) = 6.0 \text{ (isoelectric point of alanine)}$$

When a base is added to a solution of the net cationic form of alanine (initially at pH 0, for example), the first proton removed is the carboxylic acid proton, as we have said. In the case of alanine, when a pH of 2.3 is reached, the acid proton will have been removed from half of the molecules. This pH represents the  $\text{pK}_a$  of the alanine carboxylic acid proton, as can be demonstrated using the Henderson-Hasselbalch equation. The Henderson - Hasselbalch equation shows that for an acid (HA) and its conjugate base ( $\text{A}^-$ ),

$$pK_a = pH + \log \frac{[HA]}{[A^-]}$$

When the acid is half neutralized,

b) Co-polymers are another type of polymer. These contain more than one sub-unit (or monomer).

Example:

In the above example styrene and maleic anhydride monomers alternate. Co-polymer can be a block co-polymer.

Example:

Co-polymers can be random as well.

— B — A — A — B — A — B — B — A — B — A — B — B — A —

A and B are monomers.

6. There are many polymers in nature.

Example: Cellulose, starch, pepsin, insulin, egg albumin, rubber, DNA (Deoxyribonucleic acid) etc. These are called Biopolymers.

Man made polymers are, Nylon, Terylene, Polythene, Polystyrene, PVC (Polyvinyl chloride), Bakelite, Perspex, Polysiloxane etc.

7. The properties of a polymer solution are strikingly different from those of a true solution. For example, when polyvinyl alcohol is added to water, it swells.

a) Its shape gets distorted and after a long time it dissolves.

b) When more of polymer is added to a given solvent, saturation point is not reached. The mixture of polymer and solvent assumes a soft dough-like consistency.

8. Addition polymers and condensation polymers are two important types of polymers.

9. Polymer can be described as linear, branched and network.

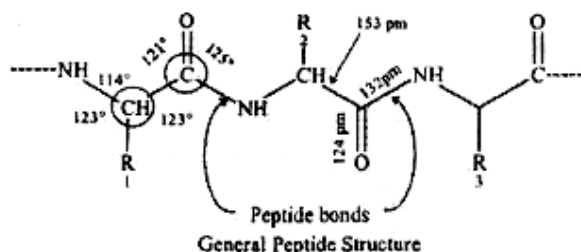
## POLYMERS AND POLYMERIZATION:

Macromolecules, both natural and man-made, owe their great size to the fact they are polymers (Greek: many parts); that is, each one is made up of a great many simpler unit - identical to each other or at least chemically similar - joined together in a regular way. They are formed by a process we touched on earlier: polymerization, the joining together of many small molecules to form very large molecules. The simple compounds from which polymers are made are called monomers.

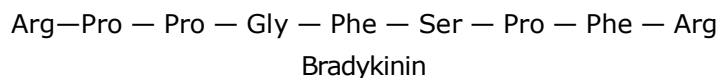
## PETIDES AND PROTEINS:

In the last section, you studied the polymers of monosaccharides which act as structural components in plants and serve as energy storage in animals. In this section, you will study another kind of natural polymers called peptides and proteins.

Peptides are biologically important polymers in which 2-amino acids are joined by the amide linkages, formed by the reaction of the carboxy group of one amino acid with the amino group of another amino acid. These amide linkages are also called peptide bonds. The general structure of a peptide is shown below:

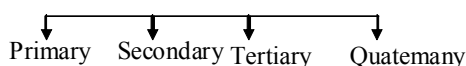


Peptides can be classified as dipeptides, tripeptides and tetrapeptides, depending on whether the number of amino acids, two, three or four, respectively. Peptides containing upto 50 amino acids are called polypeptides. Bradykinin is an important naturally occurring nonapeptide which is present in blood plasma and is involved in the regulation of blood pressure.



### Configuration of proteins :

- (a) Biological nature or function of protein was confirmed by its conformation.
- (b) This conformation is of 4 types

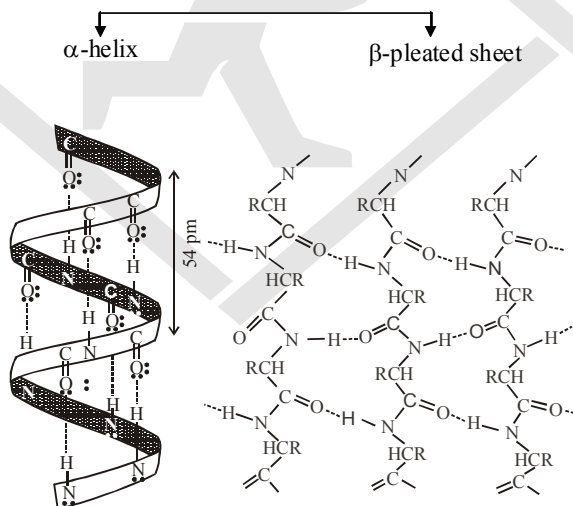


### Primary Structure :

- ⇒ This type of structure was given by **Friedrich Sanger** in 1953 in Insulin (of one chain)
- ⇒ Primary structure is conformed by a single polypeptide chain in a linear manner.
- ⇒ All amino acid are attached in a straight chain by peptide bond.
- ⇒ No biological importance & soon changed to other forms.

### Secondary Structure :

- ⇒ In it structure of straight chain from irregular changes to form coils.
- ⇒ H-bond + peptide bond present in secondary. structure.
- ⇒ This H bond is present between hydrogen of Amino group and oxygen atom carboxylic acid group.
- ⇒ This structure is of two types



#### (i) $\alpha$ -helix

- ⇒ Chain is spiral
- ⇒ 3.7 atoms in one coiling
- ⇒ Right handed circular.
- Eg. → Myosin, Keratin etc.

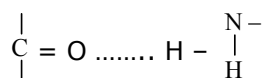


**(ii)  $\beta$ -pleated sheet**

- ⇒ Structure of protein is not arranged in a sequence.
- ⇒ Polypeptide chain are parallel to each other
- ⇒ H - bond form by near chains
- Eg. Silk fibres.

**Tertiary structure :**

- ⇒ In this structure of protein atoms are highly coiled and form a spherical form
- Ex. Albumin
- ⇒ This structure is formed by 4 regular hydrogen bonds which makes a regularity in it

**(i) Hydrogen bond :**

Hydrogen bond

- ⇒ They are formed between oxygen of acidic amino acid and H of basic amino acid.

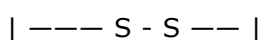
**(ii) Hydrophobic bond -**

- ⇒ Non - polar side chains of neutral amino acid tends to be closely associated with one another in proteins.
- ⇒ Present in between the amino Acid.
- ⇒ These are not true bonds.

**(iii) Ionic bond :**

Ionic bond

- ⇒ These are salt bonds formed between oppositely charged groups in side chains of Amino acids
- Eg. Aspartic acid
- Glutamic acid

**(iv) Disulphide bonds :**

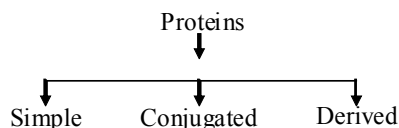
- ⇒ Relatively stable bond and thus is not broken readily under usual conditions of denaturation.
- ⇒ Formed between the -SH group of Amino acid Ex. Cystine and Methionine .

**Quaternary structure :**

- ⇒ When 2 or more polypeptide chains united by forces other than covalent bonds (i.e. not peptide and disulphide bonds) are called Quaternary structure.
- ⇒ It is most stable structure.
- Ex. Haemoglobin

**Types of proteins**

- ⇒ Classification of protein is based upon three general properties shape, Solubility and Chemical composition.

**Simple proteins**

⇒ It is formed of only Amino Acids

**Types**

⇒ 

```

graph TD
    A[Types] --> B[Fibrous]
    A --> C[Globular]
  
```

**(A) Fibrous :**

- ⇒ It is insoluble
- ⇒ It is of elongated shape.
- ⇒ It is highly resistant to digestion by proteolytic enzymes.
- ⇒ Their main function - Protection.

Ex. Collagen, Keratin etc

**(B) Globular :**

- ⇒ These are spherical and oval in shape. Chains are highly coiled
- ⇒ These are soluble.

Ex. Albumin

**Conjugated Proteins**

- ⇒ These are complex proteins in which protein molecule is combined with characteristic non-amino acid substance.
  - ⇒ Non-amino acid or Non - Protein part is called as prosthetic group
- Ex. Nucleoproteins  
(Protein + Nucleic acid),  
Phosphoproteins (Protein +  $(\text{PO}_3)^{2-}$ )  
Eg. → Casein of milk., Vitelline of egg - yolk

**Derived proteins :**

- (a) These are obtained as a result of partial hydrolysis of natural proteins.  
Eg. → Proteose, Metaproteins, Peptones

**(b) Denaturation of Proteins**

When a protein in its native form, is subjected to a physical change like change in temperature, or a chemical change like change in pH, the native conformation of the molecule is disrupted and proteins so formed are called denatured proteins.

The denaturation may be reversible or irreversible. The coagulation of egg on boiling is an example of irreversible protein denaturation.

However, it has been shown now that in some cases, the process is actually reversible. The reverse process is called **renaturation**.

**Test of Protein :**

- (a) With conc.  $\text{HNO}_3$  on heating give yellow ppt. Which on more heating give solution On adding  $\text{NH}_4\text{OH}$  Red colour appears. It is **Xanthoprotic test**.
- (b)  $(\text{NH}_4\text{OH}) + \text{dil. CuSO}_4$  protein give Blue violet colour. It is a **biurete test**.

- (c) **Millon reaction.** Proteins on adding Millon's reagent (a solution of mercuric and mercurous nitrates in nitric acid containing a little nitrous acid) followed by heating the solution give red precipitate or colour.
- (d) **Ninhydrin reaction.** Proteins, peptides and  $\alpha$ -amino acids give a characteristic blue colour on treatment with ninhydrin.

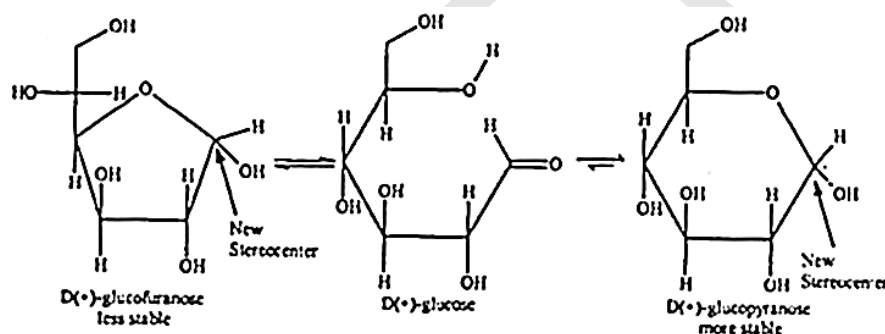
### Biological Importance of protein :

- Component of plasma membrane.
- All enzymes are protein.
- Many hormones are protein.
- Antigen and antibody are protein.
- Actin and myosin protein are important in muscle contraction.
- Proteins are important in growth, regeneration and repairing.
- Calorific value 4.0 kcal.

## SOLVED SUBJECTIVE PROBLEMS

**Problem 1:** Write the hemiacetal formation for glucose.

**Solution:**

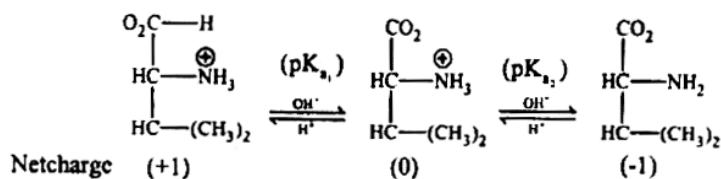


**Problem 2:** The  $pK_a$  of the carboxyl group in an amino acid valine,  $(CH_3)_2CHCH(NH_2)(COOH)$  is 2.31 and the  $pK_a$  for the amino group of the same amino acid is 9.69. compute the Isoelectric point ( $pI$ ) for valine and draw the structure of this amino acid when the pH of the solution equals  $pI$ . Also draw the structures of valine that predominate at  $pH = 2$  and  $pOH = 2$ .

**Solution:** The isoelectric point ( $pI$ ) is the pH at which the amino acid exists only as a dipolar ion with net charge zero.

$$\text{At isoelectric point, for a neutral amino acid, } pI = \frac{(pK_{a_1} + pK_{a_2})}{2}$$

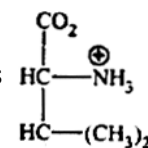
The dissociation of cationic form of valine can be represented as



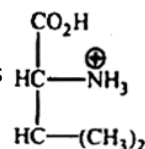
The species with zero net charge exists between species with (+1) and (-1) net charges.

$$pI = \frac{(pK_{a1} + pK_{a2})}{2} = \frac{9.69 + 2.31}{2} = 6$$

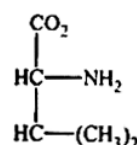
When the pI of the solution equals to pI, the structure of valine is



When the pH of the solution is two, the structure of valine is



When the pH of the solution is 12, the structure of valine is



**Problem 3:** Sucrose on hydrolysis yields a mixture which is

- (a) Optically inactive (b) Dextrorotatory (c) Laevorotatory (d) Racemic

**Solution: (c)** Sucrose on hydrolysis yields equimolar mixture of D-(—)-fructose and D-(+)-glucose. Since specific rotation of (—)-fructose is greater than (+)-glucose the mixture is laevorotatory.

**Problem 4:** A high molecular weight molecule which does not contain repeating structural units is called a

- (a) Polymer (b) Macromolecule (c) Both (a) and (b) (d) None of these

**Solution: (b)** A polymer has always repeating structural units derived from monomer. For example proteins and nucleic acid are regarded as macromolecules, but not polymers because their molecules do not contain repeating structural units. All polymers are macromolecules, but all macromolecules are not polymers.

**Problem 5:** The force of attraction between the neighbouring peptide chains is

- (a) van der Waal's force (b) Covalent bond (c) Hydrogen bond (d) Peptide linkage

**Solution: (c)** Neighbouring peptide chains are held by hydrogen bonds between —CO— and —NH—.

**Problem 6:** Peptides on hydrolysis give

- (a) Ammonia (b) Amines (c) Amino acids (d) Hydroxy acids

**Solution: (c)** Peptides are formed by condensation of  $\alpha$ -amino acids. Therefore, on hydrolysis they yield  $\alpha$ -amino acids.

**Problem 7:** An example of a condensation polymer is

- (a) PVC (b) terylene (c) polypropylene (d) polystyrene

**Solution: (b)** In condensation polymerization, a series of condensation reactions between the (generally two) monomers containing atleast two functional groups each occur with the loss of a small molecule such as  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$  or  $\text{HX}$  ( $\text{X}$  = halogen). Terylene is a condensation polymer of ethylene glycol and terephthalic acid.

**Problem 8:** Suggest a mechanism for the process. Is polymerisation of the chain reaction or step reaction type?

**Problem 9:** Although both polymers are prepared by free radical processes, poly (vinyl chloride) is amorphous and poly (vinylidene chloride) (saran) is highly crystalline. How do you account for the different? (vinylidene chloride is 1,1-dichloroethene).

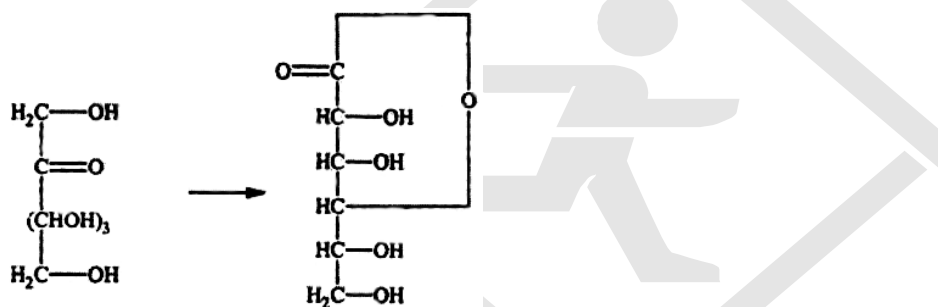
**Solution:** As poly (vinyl chloride) is able to show stereoisomerism and further it is formed by a free radical process, it is atactic (chlorine atoms (distributed randomly), the molecules fit together poorly.

Poly (vinylidene chloride) has two identical substituents on each carbon and the chains fit together well.

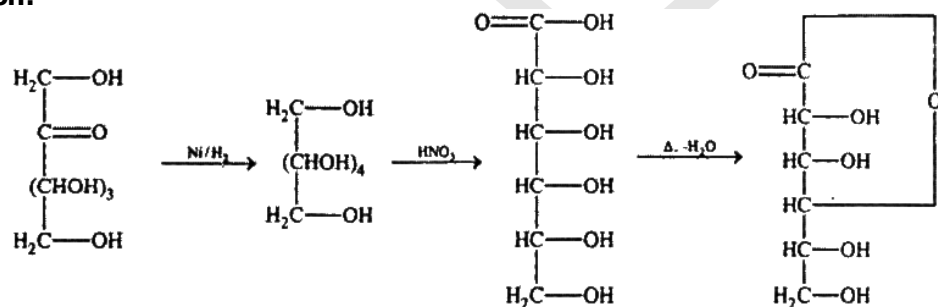
**Problem 10:** Compound A  $C_5H_{10}O_4$  is oxidized by  $Br_2 - H_2O$  to the acid,  $C_5H_{10}O_5$ . (A) Forms a triacetate ( $Ac_2O$ ) and is reduced by HI to n-pentane. Oxidation of (A) with  $HIO_4$  gives, among other product, 1 molecule of  $CH_2O$  and 1 molecule of  $HCO_2H$ . What are the possible structures of (A) and how could you distinguish between them?

**Solution:** (A) is an aldehyde, contains three hydroxyl groups and the carbon skeleton consists of five carbon atoms in a straight chain. Also, the formula  $C_5H_{10}O_4$  therefore suggests that (A) is a deoxy-sugar. If we now try to work out the possibilities based directly on the periodic oxidation of (A), we shall find it.

**Problem 11:** Convert



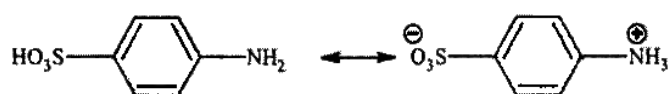
**Solution:**



**Problem 12:** i) Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acid.

ii) Sulphanilic acid is not soluble in organic solvents.

**Solution:** i) Sulphanilic acid exist as Zwitterion

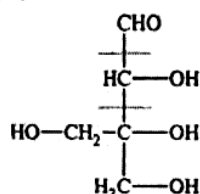


The weakly acidic  $-\text{NH}_3^+$  transfers  $\text{H}^+$  to  $\text{OH}^-$  to form a soluble salt,  $\text{P}-\text{NH}_2-\text{C}_6\text{H}_4-\text{SO}_3^-\text{Na}^+$  on the other hand  $-\text{SO}_3^-$  is too weakly basic to accept  $\text{H}^+$  from strong acids.

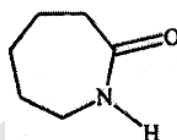
iii) Due to its ionic character it is insoluble in organic solvents.

**Problem 13:** Compound (A)  $\text{C}_5\text{H}_{10}\text{O}_7$  give a tetra-acetate with  $\text{Ac}_2\text{O}$  and oxidation of (A) with  $\text{Br}_2 - \text{H}_2\text{O}$  gives an acid,  $\text{C}_5\text{H}_{10}\text{O}_6$ . Reduction of (A) with HI and red phosphorous gives 3-methylbutane. What is structure of (A) ?

**Solution:** The formation of tetracetate indicates of 4OH group and oxidation with bromine water indicates presence of CHO group. Reduction with red phosphorous and HI indicates presence of one carbon in the side chain. Thus, the structure of (A) would be

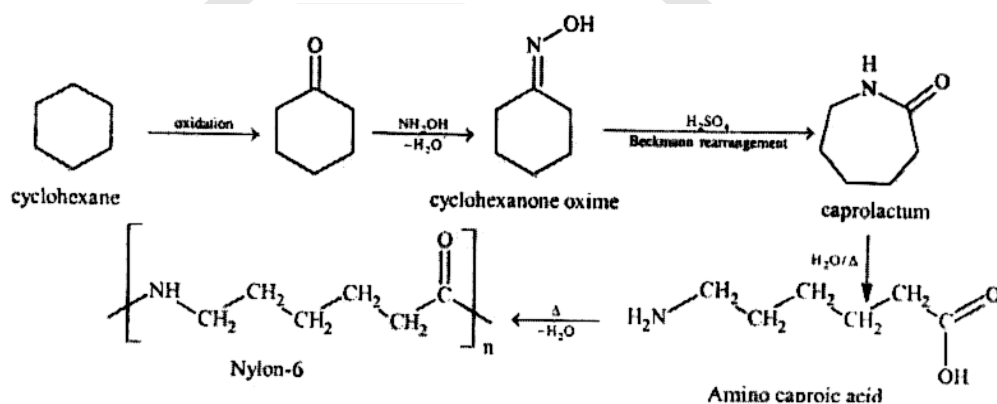


**Problem 14:** What is the structure of nylon-6, made by alkaline polymerisation of caprolactum ?



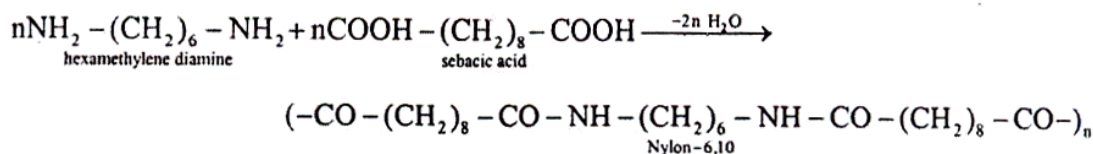
**Solution:** The configuration of these carbons which are unchanged in the reactions, must be identical in order to get the same osazone.

a) **Nylon-6:** Another polymer of this class is nylon-6. It is a monomer of caprolactum which is obtained from cyclohexane.



It used for making tyre cords, fabrics and ropes.

b) **Nylon-6, 10:** A polymer of hexamethylene diamine (six carbon atoms) and sebacic acid (ten carbon atoms).





Here aldohexose reacts with one molecule of phenylhydrazine which condenses with the aldehyde group to give phenylhydrazone. When warmed with excess of phenyl hydrazine, the secondary alcoholic group adjacent to the aldehyde group is oxidised by another molecule of phenylhydrazine, to a ketonic group. With this ketonic group, the third molecule of phenylhydrazine condenses to give osazone. The phenylhydrazinyl group is transferred from osazone to  $C_6H_5CHO$  giving  $C_6H_5CH=N.NHC_6H_5$  and a dicarbonyl compound called an osone. The more reactive aldehyde group of the osone is reduced, not the less reactive keto group and it gives the 2-ketohexose.

**Problem 19:** Starch is polymer of

- (a) Fructose                      (b) Glucose                      (c) Lactose                      (d) None

**Solution:** (b) Starch is homopolysaccharide of glucose having 24 – 30 glucose units.

**Problem 20:** The commonest disaccharide has the molecular formula

- (a)  $C_{10}H_{18}O_9$                       (b)  $C_{10}H_{20}O_{10}$                       (c)  $C_{11}H_{22}O_{11}$                       (d)  $C_{12}H_{22}O_{11}$

**Solution:** (d) The most common disaccharide is sucrose, whose molecular formula is  $C_{12}H_{22}O_{11}$ .

**Problem 21:** The structure of glycine (amino acid) is  $H_3N^+CH_2COO^-$  (Zwitter Ion.)

Select the correct statement of the following.

- (a) Glycine, as well as other amino acids are amphoteric.  
 (b) The acidic functional group in amino acids is  $-NH_3^+$   
 (c) The basic functional group in amino acids is  $-CO_2^-$   
 (d) All the statements are correct

**Solution:** (d) Glycine and all other amino acids are amphoteric because of the presence of  $NH_2$  and  $CO_2H$  group both. The amino acid exists as Zwitter ion and acidic group is  $-NH_3^+$  while basic group is  $-CO_2^-$ .

**Problem 22:** Sugars are characterised by the preparation of osazone derivatives. Which sugar has identical osazones.

- (a) Glucose and lactose                      (b) Glucose and fructose  
 (c) Glucose and arabinose                      (d) Glucose and maltose

**Solution: (b)** The reaction with phenyl hydrazone gives same osazone because glucose and fructose differ only on carbon atoms 1 and 2 which are involved in osazone formation.

**Problem 23:** Cane sugar on hydrolysis yields

- (a) Glucose and maltose                      (b) Glucose and lactose  
 (c) Glucose and fructose                      (d) Only glucose

**Solution :** (c)  $C_{12}H_{22}O_{11} \xrightarrow[H^+]{HOH} C_6H_{12}O_6 + C_6H_{12}O_6$

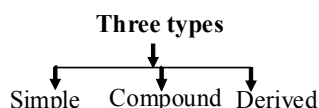
Glucose      Fructose

The process is known as inversion of cane sugar.

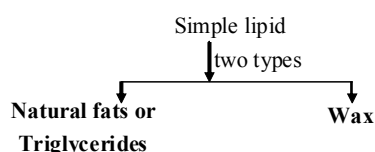


## LIPIDS

- (a) Lipids word is derived from greek word lipos which means fat.
- (b) Lipids are heterogeneous group of substances which have common property of being relatively insoluble in water and soluble in non-polar solvents such as ether, Chloroform etc.
- (c) Form 3-5% part of protoplasm.
- (d)  $H_2O \neq 2 : 1$  (different from water)
- (e) Ratio of oxygen is less.
- (f) Specific gravity  $< 1$

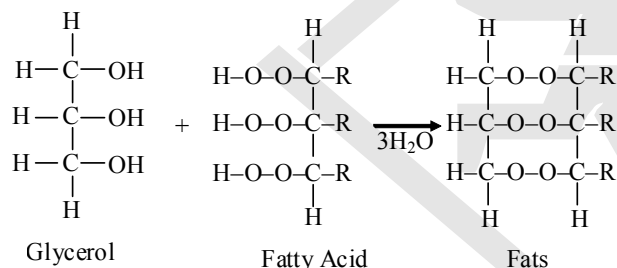


### Simple lipid :

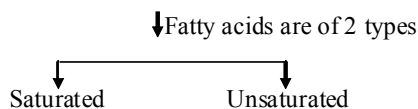


### Triglycerides

- (a) These are esters of fatty acids with glycerol.  
Ester bond is present
- (b) Synthesis is of following type-



- (c) Fatty acids which occur in natural fats usually contain an even number of carbon atoms (4 to 30) in straight chains.
- (d) Simplest fatty acid  $\text{HCOOH}$ .
- (e) More complex fatty acid are formed by successive addition of  $-\text{CH}_2$  groups.



### (i) Saturated :

- ⇒ Only single bond is present in them.
- ⇒ First member is  $\text{CH}_3\text{COOH}$ .

#### Other examples :

- ⇒ Palmitic acid -  $\text{C}_{15}\text{H}_{31}\text{COOH}$   
 $\rightarrow \text{CH}_3(\text{CH}_2)_{14}\text{COOH}$
- ⇒ Stearic acid -  $\text{C}_{17}\text{H}_{35}\text{COOH}$   
 $\rightarrow \text{CH}_3(\text{CH}_2)_{16}\text{COOH}$
- ⇒ Palmitic and stearic acid is found in fats of animals in less amount.

- ⇒ These are solid and are found in fats.
- (ii) Unsaturated :**
- ⇒ Double bond is present in these fatty acid chain.
- ⇒ These are liquids at room temperature. Found in Oils.
- ⇒ These are of two types
- Monounsaturated** - 1 Double bond is present
- Eg. Oleic acid.
- ⇒ Oleic acid is present in more amount in nature.
- Polyunsaturated** - More than two double bond
- Eg. Linoleic acid with two double bonds
- Linoleic acid with three double bonds
- Arachidonic acid with four double bonds (Groundnut)

**Wax :**

- ⇒ These are esters of other alcohols of high molecular weight instead of glycerols.
- ⇒ These are insoluble in water.
- ⇒ These are monohydric alcohols.
- ⇒ Some examples of waxes -
- Myricyl palmitate (Honeybee wax) Cetyl palmitate (Dolphin and whale wax)
- Cerumen (ear wax)

**Compound Lipid-** Are of 4 types :

(a) Phospholipids.

(b) Glycolipids.

**Phospholipids :**

Phosphorous is present.

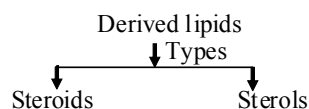
ex. cell wall

**Glycolipids**

- ⇒ Lipid + Sugar = Glycolipids
- ⇒ Present in brain, Adrenal glands, kidney, WBC liver, thymus, Spleen, Lungs, egg yolk
- ⇒ Glycolipids = 2 Fatty acid + 1 sphingosine + 1 galactose.

**Derived lipids**

- ⇒ By hydrolysis of fats they are obtained



**Steroids :**

- ⇒ These are different from other fats.
- ⇒ It is insoluble in water.

**(i) Bile acids :**

⇒ Present in secretion of liver.

**(ii) Sex hormones :**

⇒ These are androsterones.

**(iii) Adrenal hormone-** Eg : Aldosterone**Sterols :**

⇒ They have -OH groups.

⇒ They are complex monohydroxy alcohols.

**(i) Cholesterol** - It is widely distributed in all cells of body.**Biological importance of Fat :**

⇒ It is source of energy.

⇒ It is important for absorption of vitamin A, D, E and K.

⇒ It is important component of plasma membrane.

⇒ It act as shock absorber of body.

⇒ Calorific value 9.3 kcal.

**NUCLEIC ACID**

(a) These are special type of acids which are present in nucleus & cytoplasm.

(b) Control the metabolic activities of cell.

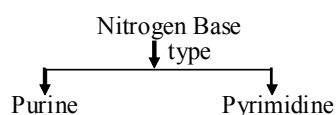
(c) They are also found in Mitochondria, centriole and chloroplast.

**Types** → These are of 2 types

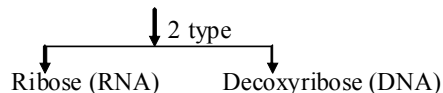
→ DNA (Deoxyribonucleic acid)

→ RNA (Ribonucleic acid)

(d) **Fischer** discovered Nitrogen bases in 1888



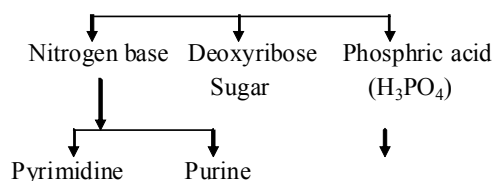
(e) **Levan** found sugar

**Deoxyribosenuclie Acid (D.N.A.) :**

(a) It is found in Nucleus.

(b) They on pneumococcus bacteria.

(c) DNA made up of 3 units-



- (i) Thymine                      (i) Adenine
- (ii) Cytosine                  (ii) Guanine

(d) **Nucleoside**

When nitrogen base combined with deoxyribose sugar it constitute a nucleoside.

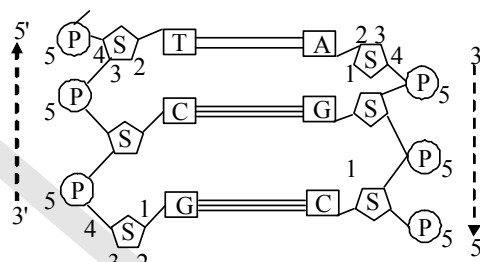
S.No.	Deoxyribonucleoside
1	Adenine + Deoxyribose → Deoxyadenosine
2	Guanine + Deoxyribose → Deoxyguanosine
3	Cytosine + Deoxyribose → Deoxycytidine
4	Thymine + Deoxyribose → Deoxythymidine

(i) **Nucleotide**

- (a) Nitrogen base+Sugar+Phosphate → Nucleotide
- (b) Nucleotide is a unit of DNA.
- (c) All nucleotides combined and form a chain called polynucleotides by which RNA and DNA formed.

**Structure of DNA**

- (a) Double Helical model of DNA was proposed by biochemist **J.D.Watson**, British chemist **FHC Crick** in 1953.
- (b) DNA in double stranded structure is made up of two chains of polynucleotides.
- (c) DNA is a polymer of Nucleotide.
- (d) Nucleotide are joined by 3' → 5' phosphodiester bonds.
- (e) Sugar and phosphorous are alternately arranged.
- (f) In both chains, in between A and T, 2 Hydrogen bonds are present while in C and G 3H bonds are present.  
(A = T) (C ≡ G)
- (g) A always attach with T while C always attaches with G.
- (h) Purine and pyrimidine are found in ratio 1 : 1. cells.
- (i) DNA is attached with histone protein.
- (j) In prokaryotic cell and mitochondria circular DNA is present.



**Function of DNA**

(i) **Self - Replication or self -Duplication**

DNA has the property of self - replication . It is therefore a reproducing molecule. This unique property of DNA is at the root of all reproduction. Through its replication, **DNA is acts as the key to heredity.** In the replication of DNA, the two strands of a double helix unwind and separate as a template for the formation of a new complementary strand.

(ii) **Protein Synthesis**

The specific sequence of base pair in DNA represents coded information for the manufacture of specific proteins. These code instructions first are transcribed into the matching nitrogen- base sequences within mRNA and the instructions in such RNA subsequently are translated into particular sequence of amino acid units within the polypeptide chains and proteins.

The major steps in the utilization of the genetic information can be represented as :

D N A  $\xrightarrow{\text{Replication}}$  D N A  $\xrightarrow{\text{Transcription}}$  R N A  $\xrightarrow{\text{Translation}}$  Protein

**Ribonucleic Acid (RNA) :**

- ⇒ Found in cytoplasm as well as in nucleus.
- Cytoplasm → In the ribosome (higher amount)

**Chemical Nature :**

- ⇒ Ribonucleic acid is a polymer of purine and pyrimidine ribonucleotides linked by 3' → 5' phosphodiester bridges. The number of nucleotides in RNA ranges from as **few as 75 to many thousands**. Although sharing many features with DNA, RNA possesses several specific differences.
- ⇒ As indicated by its name, sugar in RNA to which the phosphate and nitrogen-bases are attached is ribose rather than the deoxyribose of DNA.
- ⇒ Although RNA contains the ribonucleotides of adenine, guanine, and cytosine, it does not possess thymine. Instead of thymine, RNA contains the ribonucleotides of uracil. Thus the pyrimidine components of RNA differ from those of DNA.
- ⇒ RNA exists basically **as a single-stranded molecule** rather than as a double-stranded helical molecule, as does DNA. However the single strand of RNA is capable of folding back on itself like a hairpin and thus acquiring double-stranded characteristics. In these regions, A pairs with U and G pairs with C.

Thus a given segment of a long RNA molecule might, for example, be represented as follows.

P-R-P-R-P-R-P-R-P-R

A	U	G	G	C

- ⇒ where R stands for ribose ; A, U, G, and C for Adenine, Uracil, Guanine and Cytosine respectively.

**Types of RNA and their Functions :**

There are 3 main types of RNA molecules

- (i) Messenger RNA (mRNA)      (ii) Transfer RNA (tRNA)      (iii) Ribosomal RNA (rRNA)

**(i) Messenger RNA (mRNA)**

- ⇒ This type of RNA consists of **single strand** of variable length and serves as a template for protein synthesis. Codon in the chromosomes.
- ⇒ mRNA forms complementary copy of DNA as it carries **chemical messages in the form of nitrogen-base sequence from the nucleus to the ribosomes**, i.e. from **DNA to cytoplasm where proteins are synthesized**. Therefore, it is called messenger RNA or mRNA
- ⇒ mRNA is synthesised from DNA in the nucleus.
- ⇒ It is called **transcription**.

**(ii) Ribosomal RNA**

- ⇒ A ribosome is a cytoplasmic nucleoprotein structure which serves as the organellar machinery for protein synthesis from mRNA templates.

- ⇒ On the ribosome, the mRNA and tRNA molecules interact to translate into a specific protein molecule the information transcribed from the DNA.
- ⇒ rRNA constitutes the largest part of total RNA (Highest) - 80%

**(iii) Transfer RNA (RNA) :**

- ⇒ These are also called **Soluble RNA**.
- ⇒ Single stranded.
- ⇒ 10-15% of the total RNA.
- ⇒ **Size - Smallest** → 75 - 80 nucleotides only.
- ⇒ **Synthesis** - Within **nucleus** from **DNA**.
- Function**- It transports amino acid from cytoplasm to the site of protein synthesis.

## ENZYMES

Proteins which are used as a catalyst in biochemical reaction is known as biocatalysts.

### Specific characteristics

Enzymes have following two specific character as :

- (i) Specificity (ii) Efficiency

### Specificity of enzymes

- (a) Generally one enzyme can catalyze only one biochemical reaction.
- (b) It can increase rate of reaction upto  $10^{20}$  times.
- (c) In some cases one enzyme can catalyze more than one reaction and one reaction can be catalyzed by more than one enzyme.  
eg. Enzyme present in Yeast (Zymase) can ferment both glucose and fructose into alcohol and also cane-sugar can be hydrolysed by invertase and sucrase enzymes.

### Efficiency of enzymes

- (a) One molecule of enzyme can convert millions of substrate molecules into product per second.  
eg. Carbonic anhydrase enzyme present in red blood cells has a highest turn over number.
- (b) With having tertiary structure it can be collected as crystals.  
Enzymes are denatured at higher temperature.
- (c) Enzyme can be stored at low temperature as they are inactivated.

### Importance of enzymes

In the thousands of enzymes presents in body if even a single enzyme would be absent or damaged than complex disease in results.

eg. Scarcity of **Phenylalanine** hydroxylase enzyme in human body is result in **Phenylketonuria** disease.

### Factors affecting enzyme action :

- (i) **Optimum temperature and pH.** Enzyme catalysed reactions have maximum rate at physiological pH of around 7.4 and human body temperature of  $37^{\circ}\text{C}$  ( $310\text{ K}$ ) under one atmosphere pressure. In fact, as the temperature or pH is increased, the rate rises to a maximum (at  $37^{\circ}\text{C}$  or  $\text{pH} = 7.4$ ) and then falls off.
- (ii) **Enzyme activators (co-enzymes).** The activity of certain enzymes is increased in the presence of certain substances, called co-enzymes. It has been observed that if a protein contains a small amount of vitamin as the non-protein part, its activity is enhanced considerably. The activators are generally metal ions such as  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  etc. These metal ions are weakly bonded to the enzyme molecules and increase their catalytic activity. For example, the enzyme, amylase, in presence of  $\text{NaCl}$ , which provides  $\text{Na}^+$  ion, shows a very high catalytic activity.
- (iii) **Enzyme inhibitors and poisons.** Just as in the case of catalysts, the activity of enzyme is slowed down in the presence of certain substance. Such substances are called inhibitors or poisons. They act by combining with the active functional group thereby reducing or completely destroying the catalytic activity of the enzymes. The use of many drugs is on account of their action as enzyme inhibitors in our body.

## NUTRIENTS

### Sodium, Potassium and Chlorine

- (i)  $\text{Na}^+$  is the principal mineral cation in the extracellular fluid.
- (ii)  $\text{K}^+$  is the principal cation inside the cell.
- (iii)  $\text{Cl}^-$  is the principal mineral anion in the ECF.
- (iv)  $\text{Na}^+$  and  $\text{K}^+$  are essential to the maintenance of water balance and acid-base balance.
- (v)  $\text{Na}^+$  and  $\text{K}^+$  are important in nerve impulse transmission.

### Calcium and Phosphorus

- (i) Calcium and phosphorus are deposited in bones and teeth to give them strength and rigidity.

- (ii)  $\text{Ca}^{2+}$  is also essential for blood coagulation, neuromuscular function, cardiac function and actions of many enzymes and hormones.
- (iii) Phosphorus enters into many compounds such as nucleic acids and phospholipids, many coenzymes and high energy compounds like ATP.
- (iv) Calcium plays an essential role in sustaining intestinal peristalsis and growth of body tissues.

**Iron**

- (i) Iron is required for haemoglobin synthesis.
- (ii) Iron is essential both for transportation of oxygen to tissues and for operation of oxidative systems within the tissue cells.

**Magnesium**

- (i) Magnesium is required as a catalyst for many intracellular enzymatic reactions, particularly those relating to carbohydrate metabolism.
- (ii) Mg is the central metal atom in chlorophyll

**Iodine**

Iodine is used in the synthesis of thyroid hormones.

**Zinc**

- (i) Zinc is a constituent of carbonic anhydrase, present in RBCs helping in  $\text{CO}_2$  transport.
- (ii) Zinc is a component to lactic dehydrogenase, important for the interconversion between pyruvic acid and lactic acid
- (iii) Zinc is a component part of some peptidases and therefore is important for digestion of proteins in the alimentary canal

**Cobalt**

- (i) Cobalt helps in erythropoiesis and in the activities of some enzymes.
- (ii) It is present in vitamin  $\text{B}_{12}$

**Copper**

- (i) Copper helps in the utilisation of iron.
- (ii) Copper deficiency may produce anaemia because of failure in iron utilisation.

**Molybdenum**

- (i) Molybdenum is a constituent of oxidase enzymes (**xanthine oxidase**)
- (ii) Molybdenum plays an important role in biological **nitrogen** fixation

**Fluorine**

- (i) Fluorine maintains normal dental enamel and prevents dental caries.
- (ii) Excessive intake of fluorine cause fluorosis characterized by mottled teeth and enlarged bones.

## VITAMINS

It has been observed that certain organic compounds are required in small amounts in our diet but their deficiency causes specific diseases. These compounds are called vitamins.

**Classification of Vitamins**

Vitamins are classified into two groups depending upon their solubility in water or fat.

**(i) Fat soluble vitamins:**

Vitamins which are soluble in fat and oils. But insoluble in water are kept in this group. These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.

**(ii) Water soluble vitamins:**

B group vitamins and vitamin C are soluble in water so they are grouped together. Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and can not be stored (except vitamin B<sub>12</sub>) in our body.

Some important vitamins, their sources and diseases caused by their deficiency are listed in table.

Sr. No.	Name of Vitamins	Source	Deficiency Diseases
1	Vitamin A (Retinol)	Fish liver oil, carrots, butter and milk	Xerophthalmia (hardening of cornea of eye) Night blindness
2	Vitamin B <sub>1</sub> (Thiamine)	Yeast, milk, Green Vegetables and cereals and grams	Beri beri (loss of appetite, retarded growth)
3	Vitamin B <sub>2</sub> (Riboflavin)	Milk, egg white, liver, Kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin
4	Vitamin B <sub>6</sub> (Pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions
5	Vitamin B <sub>12</sub> (Cyanocobal-amine)	Meat, fish, egg and curd	Pernicious anaemia (RBC deficient in haemoglobin)
6	Vitamin C (Ascorbic acid)	Citrus fruits, amla and green leafy vegetables	scurvy (bleeding gums)
7	Vitamin D (Calciferol)	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteomalacia (soft bones and joint pain in adults)
8	Vitamin E or Tocopherol ( $\alpha$ , $\beta$ and $\gamma$ ) or Antisterility factor	Eggs, Milk, Fish, Wheat germ oil cotton seed oil etc.	Sterility (loss of sexual power and reproduction)



## POLYMERS

The term polymer is used to describe a very large molecule that is made up of many repeating small molecular units. These small molecular units from which the polymer is formed are called monomers. The chemical reaction that joins the monomers together is called polymerisation. Starting from  $n$  molecules of a compound  $M$ , linking in a linear manner will form polymer  $x-M-(M)_{n-2}-M-y$ . The nature of linkages at the terminal units i.e.  $M-x$  and  $M-y$  depends upon the mode of reaction used in making the polymers.

### Homopolymers and Copolymers

Polymers which are formed by only one type of monomer are called Homopolymers. Some examples of homopolymers and their monomers are given below :

Homopolymer	Monomer
Starch	Glucose
Cellulose	Glucose
Glycogen	Glucose
Dextrin	Glucose
Inulin	Fuctose
Polyethylene	Ethylene
Polyvinyl chloride	Vinyl chloride
Teflon	Tetrafluoro ethylene
Nylon-6	Caprolactam
Polystyrene	Styrene
Orlon (Acrilan)	Acrylonitrile
Plexiglas (Lucite)	Methyl methacrylate
Polyvinyl acetate	Vinyl acetate

Polymers, which are formed by more than one type of monomers are known as copolymers. Some examples are given below in the table:

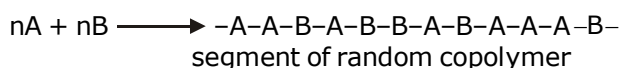
Copolymer	Monomers
Saran	Vinyl chloride and vinylidene chloride
SAN	Styrene and acrylonitrile
ABS	Acrylonitrile, butadiene and styrene
Butyl rubber	Isobutylene and Isoprene
Buna-S, SBR	Styrene and Butadiene
Buna-N, NBR	Acrylonitrile and Butadiene
Nylon-66	Hexamethylen diamine and Adipic acid
Terylene	Terephthalic acid and ethylene glycol

### Types of copolymers

Depending upon the distribution of monomer units, the following types of copolymers are possible.

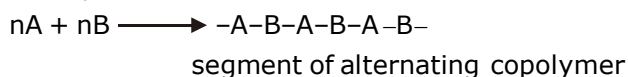
#### (1) **Random Copolymer**

If the monomer units have random distribution throughout the chain, it is called random copolymer. For example, if the monomer A and monomer B undergo copolymerisation then the structure of the random copolymer is



#### (2) **Alternating Copolymer**

If the two monomer units occur alternatively throughout the polymer chain, it is said to be alternating copolymer. For example,

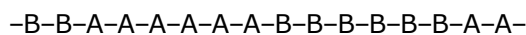


The exact distribution depends upon the proportion of the two reactant monomers and their relative reactivities. In practice neither perfectly random nor perfectly alternating copolymers are usually formed. However, most copolymers tend more towards alternating type but have many random imperfections.

**(3) Block Copolymer**

Polymers in which different blocks of identical monomer units alternate with each other are called block copolymers.

For example,

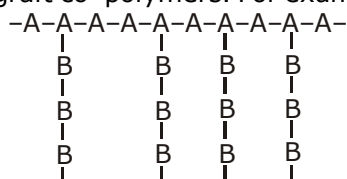


segment of block copolymer

Block copolymer can be prepared by initiating the radical polymerisation of one monomer to grow homopolymer chains, followed by addition of an excess of the second monomer.

**(4) Graft Copolymer**

Polymers in which homopolymer branches of one monomer unit are grafted onto a homopolymer chain of another monomer unit are called graft co-polymers. For example:



(Segment of a graft copolymer)

Graft copolymers are prepared by  $\gamma$ -irradiation of a homopolymer chain in the presence of a second monomer. The high energy radiation knock out H-atoms from the homopolymer chain at random points thus generating radical sites that can initiate polymerisation of the second monomer.

**CLASSIFICATION OF POLYMERS**

Polymers are classified in following ways:

**(I) CLASSIFICATION BASED UPON SOURCE****(1) Natural polymers**

Polymers which are obtained from animals and plants are known as natural polymers, Examples of natural polymers are given below.

**Natural polymer**

- |                                      |                         |
|--------------------------------------|-------------------------|
| 1. Polysaccharide                    | <b>Monomers</b>         |
| 2. Proteins                          | Monosaccharide          |
| 3. Nucleic acid                      | $\alpha$ -L-Amino acids |
| 4. Silk                              | Nucleotide              |
| 5. Natural Rubber (cis polyisoprene) | Amino acids             |
| 6. Gutta purcha (trans polyisoprene) | Isoprene                |

Natural polymers which take part in metabolic processes are known as biopolymers. Examples are polysaccharides, proteins, RNA and DNA.

**(2) Semisynthetic polymers**

Polymers which are prepared from natural polymers are known as semisynthetic polymers. Most of the semisynthetic polymers are prepared from cellulose.

Examples are: cellulose acetate, cellulose nitrate, cellulose xanthate and Rayon.

**(3) Synthetic polymers**

Man-made polymers, i.e. polymers prepared in laboratory are known as synthetic polymers. Example are : PVC, polyethylene, polystyrene, nylon-6, nylon-66, nylon-610, terylene, synthetic rubbers etc.

**(II) CLASSIFICATION BASED UPON SHAPE****(1) Linear polymers**

Polymer whose structure is linear is known as linear polymer. The various linear polymeric chains are stacked over one another to give a well packed structure.



The chains are highly ordered with respect to one another. The structure is close packed in nature, due to which they have high densities, high melting point and high tensile (pulling) strength. Linear polymers can be converted into fibres.

**Note :**

- (i) All fibers are linear polymers. Examples are cellulose, silk, nylon, terylene etc.
- (ii) Linear polymers may be condensation as well as addition polymers. Examples are cellulose, Polypeptide, nucleic acid, nylon, terylene etc.

**(2) Branched chain polymers**

Branched chain polymers are those in which the monomeric units constitute a branched chain. Due to the presence of branches, these polymers do not pack well. As a result branched chain polymers have lower melting points, low densities and tensile strength as compared to linear polymers.



**(3) Cross-linked or Three Dimensional network polymers**

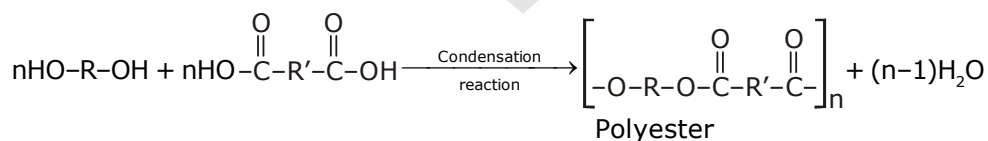
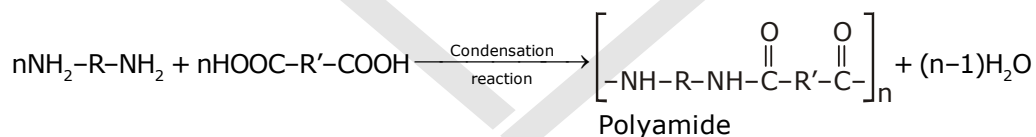
In these polymers the initially formed linear polymeric chains are joined together to form a three dimensional network structure. These polymers are hard, rigid and brittle. Cross-linked polymers are always condensation polymers. Resins are cross linked polymers.



**CLASSIFICATION BASED UPON SYNTHESIS**

**(1) Condensation polymerisation**

- (i) They are formed due to condensation reactions.
- (ii) Condensation polymerisation is also known as step growth polymerisation.
- (iii) For condensation polymerisation, monomers should have at least two functional groups. Both functional groups may be same or different.
- (iv) Monomers having only two functional group always give linear polymer.  
For example,



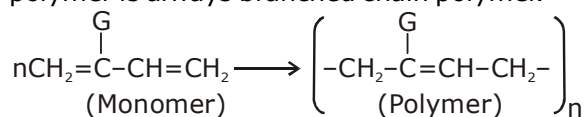
- (v) Condensation polymers do not contain all atoms initially present in the monomers. Some atoms are lost in the form of small molecules.
- (vi) Monomer having three functional groups always gives cross-linked polymer.  
Examples are : Urea-formaldehyde resin, phenol-formaldehyde resin.

**(3) Addition polymerisation**

- (i) Polymers which are formed by addition reaction are known as addition polymers.
- (ii) If monomer is ethylene or its derivative, then addition polymer is either linear polymer or branch-chain polymer.

Examples are : polystyrene, polytetrafluoroethylene, polyacrylonitrile etc.

- (iii) If monomer is 1, 3-butadiene or 2-substituted-1, 3-butadiene  $\left( \begin{array}{c} \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ | \\ \text{G} \end{array} \right)$ , then polymer is always branched chain polymer.



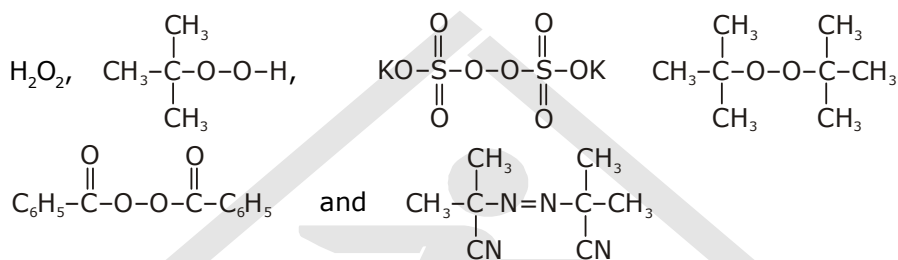
- | (Monomer)  | (Polymer)                        |
|--|----------------------------------|
| (i) G = H: 1, 3-Butadiene                                      | (i) Polybutadiene                |
| (ii) G = CH <sub>3</sub> ; 2-Methyl-1, 3-butadiene or isoprene | (ii) Polyisoprene                |
| (iii) G = Cl; 2-Chloro-1, 3-butadiene or chloroprene           | (iii) Polychloroprene (Neoprene) |

- (iv) Addition polymers retain all the atoms of the monomer units in the polymer.  
 (v) Addition polymerisation takes place in three steps: Initiation, chain propagation and chain termination.  
 (vi) Addition polymers are called as chain growth polymers.

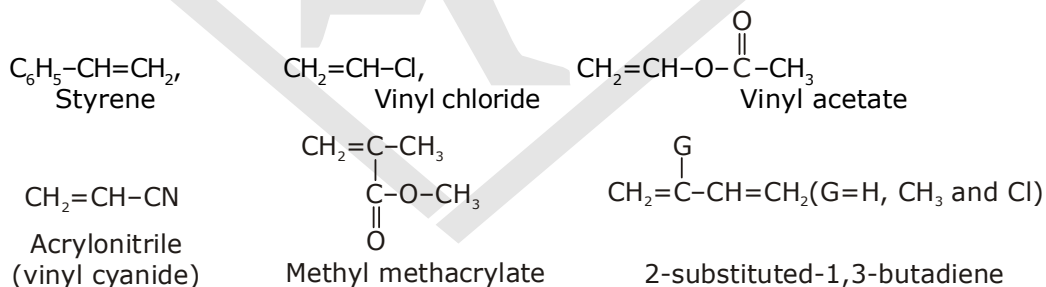
### Types of Addition Polymerization

#### (A) Radical Polymerisation:

- (i) Radical polymerisation takes place in the presence of radical initiators. The radical initiator may be any of the following :



- (ii) Reaction intermediate of radical polymerization is a free radical.  
 (iii) Radical polymerization has more chance for those monomers whose free radicals are more stable. Examples are:

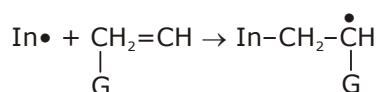


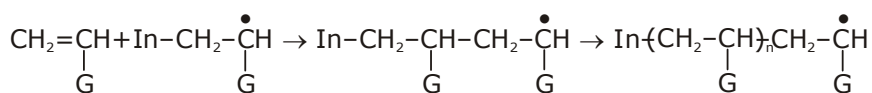
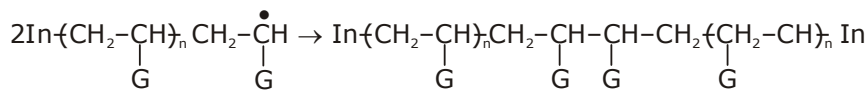
- (iv) Radical polymer has linear as well as branched chain structure  
 Most of the commercial addition polymers are vinyl polymers obtained from alkenes and their derivatives  $\text{CH}_2=\underset{\text{G}}{\text{CH}}$  [G is H, C<sub>6</sub>H<sub>5</sub>, R etc.]

This type of polymerization is performed by heating the monomer with only a very small amount of the initiator or by exposing the monomer to light. The general mode of radical polymerization of vinyl monomers is depicted below:

#### Chain initiation step :

Initiator  $\rightarrow$  In •

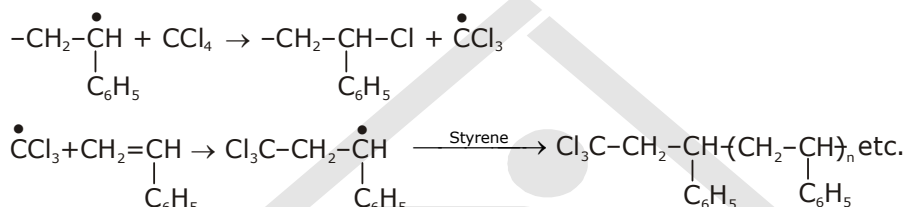


**Chain propagating step :****Chain terminating step :**

Polymer

In vinylic polymerization, various other reaction of free radicals with some other compounds present may compete with the parent addition chain reactions. One such reaction takes place with molecules that can react with the growing chain to interrupt the further growth. This leads to the lowering of the average molecular mass of the polymer. Such reagents are called as chain transfer agents and include  $\text{CCl}_4$ ,  $\text{CBr}_4$  etc.

For example, in the presence of  $\text{CCl}_4$ , styrene polymerises to form polystyrene of a lower average molecular mass which also contains some chlorine what happens here is that growing polystyrene radical which normally would add on a monomer reacts with the chain transfer agent to end the original chain and produces a new radical. The latter initiates a new polymerization chain and thereby forms a new polymer as depicted below.

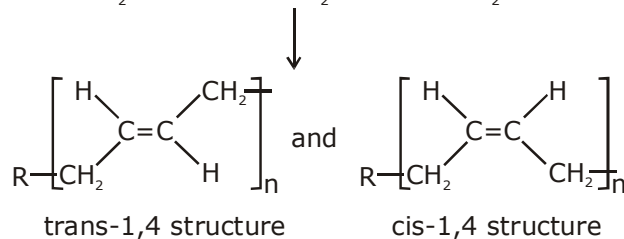
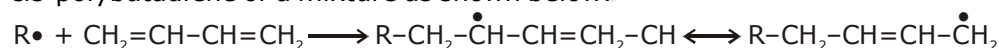


If the chain transfer agent a radical, which is highly unreactive, the reaction chain gets terminated such a compound thus inhibits or arrests polymerisation. Many amines, phenols, quinones etc. act as inhibitors. So, even traces of certain impurities, which can act as chain transfer agent or an inhibitor can interfere with the original polymerisation chain reaction. Hence, the monomers should be free from such inhibitors.

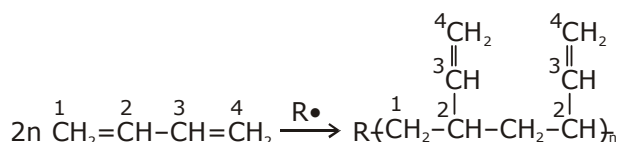
In case the alkene is a diene, the following kinds of polymerisation is possible:

**(1) 1, 4-polymerisation**

When the polymerisation takes place at  $\text{C}_1$  and  $\text{C}_4$  of butadiene, an unbranched polymer is formed. This product is different from that formed from an alkene having a double bond, which at each of its carbons is substituted by different groups and hence can exist either as trans-polybutadiene or cis-polybutadiene or a mixture as shown below.

**(2) 1, 2-polymerisation**

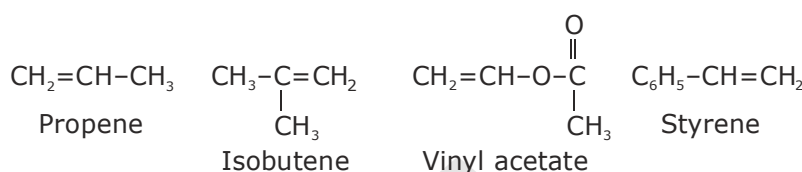
Alternatively, 1, 3-butadiene can undergo polymerisation at  $\text{C}_1$  and  $\text{C}_2$  to yield the polymeric product, polyvinyl polythene.



The double bonds in these initial polymers can be linked by further treatment with chemicals to modify the properties of the polymers. These reactions form the basis of the formation of rubber.

**(B) Cationic Polymerisation :**

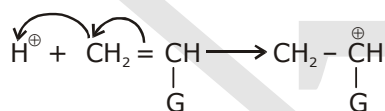
- (i) Polymerisation which is initiated by an electrophile is known as cationic polymerisation.
- (ii) Reaction intermediate of cationic polymerisation is a carbocation.
- (iii) Carbocations can undergo rearrangement leading to the formation of a more stable carbocation.
- (iv) The electrophile commonly used for initiation is  $\text{BF}_3 \cdot \text{OEt}_2$ .
- (v) Monomers that are best able to undergo polymerisation by a cationic mechanism are those with electron - donating substituents that can stabilise the carbocation. Some examples are:



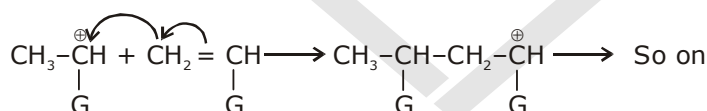
- (v) It is terminated by a base.

Thus, when the initiator is cationic in nature, it would generate a cationic intermediate on addition to the double bond for propagating the addition chain process and is termed as cationic addition polymerisation. The process is initiated by an acid. The stages of polymerisation are depicted below.

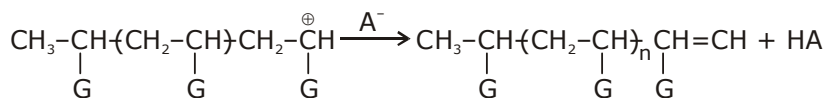
**Chain initiation step :**



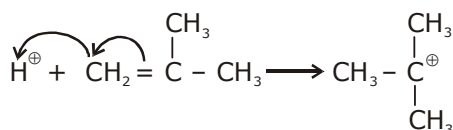
**Chain propagating step :**

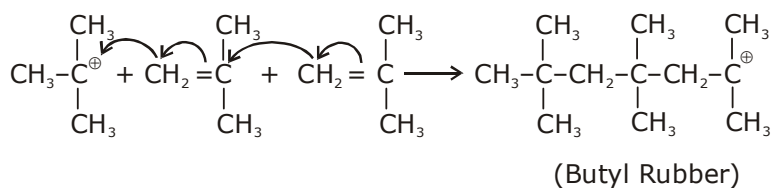


**Chain terminating step :**



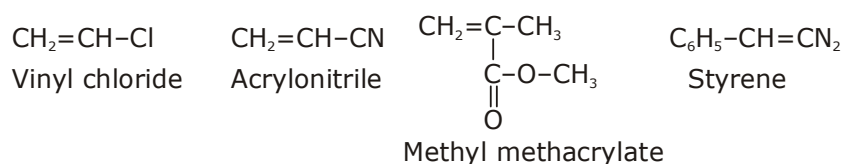
Cationic polymerisation is facilitated in monomers containing electron - releasing groups. Thus, isobutylene undergoes cationic polymerisation easily as it has two electron releasing  $-\text{CH}_3$  groups that will stabilize the intermediate carbo cation.



**(C) Anionic Polymerisation:**

- (i) Anionic polymerisation takes place in the presence of base or nucleophile, which is initiator in this polymerisation.
- (ii) Reaction intermediate in propagation steps are carboanion.
- (iii) the suitable initiator can be  $\text{NaNH}_2$  or  $\text{RLi}$ .
- (iv) Those monomers undergo anionic polymerisation reaction whose anion is stable.

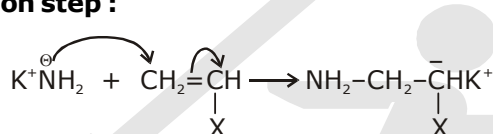
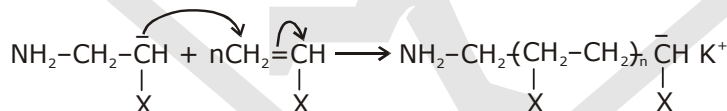
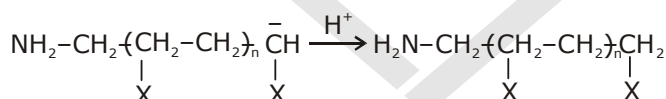
Example of monomers are:



- (v) Anionic polymerisation always give linear polymer.

- (iv) Anionic polymerisation terminated by an acid.

The formation of polystyrene from styrene in the presence of potassium amide is an important example of this category of polymerisation. The mode of anionic polymerisation is depicted below:

**Chain initiation step :****Chain propagating step :****Chain terminating step :****(D) Ziegler-Natta polymerisation :**

- (i) Addition polymerisation which takes place in the presence of Ziegler-Natta catalyst  $[(\text{C}_2\text{H}_5)_3\text{Al}$  and  $\text{TiCl}_4]$  is known as Ziegler-Natta polymerisation or co-ordination polymerisation.
- (ii) Ziegler-Natta polymerisation always gives linear, stereo-regular polymers.
- (iii) Ziegler-Natta catalyst revolutionised the field of polymer chemistry because they allow the synthesis of stronger and stiffer polymers (due to linear geometry) that have greater resistance to cracking and heat. High density polyethylene is prepared using a Ziegler-Natta catalyst.

**CLASSIFICATION BASED ON INTERMOLECULAR FORCES (SECONDARY FORCES)**

- (i) Intermolecular forces present between polymeric chains are (a) Van der Waals forces (b) Hydrogen bonds and (c) Dipole-dipole attractions.
- (ii) Mechanical properties such as tensile strength, elasticity, toughness etc. depend upon the secondary force present between the polymeric chains.
- (iii) Magnitude of secondary forces depends upon the size of the molecule and the number of functional groups along the polymeric chains.

Magnitude of secondary forces is directly proportional to the length of the polymeric chain. On the

basis of magnitude of secondary forces, polymers can be divided into the following

#### **Five categories.**

#### **(1) Elastomes**

An elastomer is a plastic that stretches and then reverts back to its original shape. It is randomly oriented amorphous polymer. It must have some cross-links so that the chains do not slip over one another. Very weak Van der Waal forces are present in between polymeric chains.

When elastomers are stretched, the random chains stretch out, but there are insufficient Van der Waal forces to maintain them in that configuration and position. When the stretching force is removed, they go back to their random shape. Elastomers have the ability to stretch out over ten times their normal length.

Important examples are vulcanized rubbers.

**Note :** Addition polymers obtained from butadiene and its derivatives are elastomers.

#### **(2) Fibres**

Fibres are linear polymers in which the individual chains of a polymer are held together by hydrogen bonds and / or dipole-dipole attraction. In the fibres, the polymeric chains are highly ordered with respect to one another.

Due to strong intermolecular forces of attraction and highly ordered geometry, fibres have high tensile strength and least elasticity. They have crystalline character and have high melting points and low solubility. Examples are cellulose, nylon, terylene, wool, silk etc.

**Note:** (i) Condensation polymers formed from bifunctional monomers are fibres in character.  
(ii) Addition polymers of alkene derivatives having strong-I group are fibres in character.

#### **(3) Thermoplastic Polymers**

Thermoplastic polymers are polymers that have both ordered crystalline regions (the regions of the polymer in which the chains are highly ordered with respect to one another) and amorphous, non crystalline regions (the regions of the polymer in which the chains are randomly oriented).

The intermolecular forces of attraction are in between elastomers and fibres. There are no cross-links between the polymeric chains. Thermoplastic polymers are hard at room temperature, but when they are heated, the individual chains can slip past one another and the polymer become soft and viscous. This soft and viscous material become rigid on cooling. The process of heating softening and cooling can be repeated as many times as desired without any change in chemical composition and mechanical properties of the plastic. As a result, these plastics can be moulded into toys, buckets, telephone and television cases.

Some common examples are : polyethene polypropylene, polystyrene, polyvinylchloride, teflon etc.

**Note :** Addition polymers obtained from ethylene and ethylene derivatives are thermoplastic polymers.

#### **(4) Thermosetting Polymers**

Polymers which become hard on heating are called thermosetting polymers. Thermosetting polymers can be heated only once when it permanently sets into a solid, which cannot be remelted by heating. Thermosetting polymers are cross-linked polymers. Greater the degree of cross- linking that exist, the more rigid is the polymer. Cross-linking reduces the mobility of the polymer chains, causing them to be relatively brittle materials, the hardening on heating is due to the extensive cross-linking between different polymer chains to give a three dimensional network solid. Examples are : phenol formaldehyde resin, urea-formaldehyde resin, melamine- formaldehyde resin.

### **DIFFERENCE BETWEEN THERMOPLASTIC AND THERMOSETTING POLYMERS**

#### **S.No. Thermoplastic polymers**

1. Soften and melt on heating and become hard on cooling i.e. process is reversible
2. Can be moulded and remoulded and reshaped.
3. They are addition polymers
4. Structure is generally linear

#### **Thermosetting polymers**

- Become hard on heating and process is irreversible.
- They can be moulded once and cannot be remoulded or reshaped.
- They are condensation polymers.
- Structure is cross - linked.

### **RUBBER**

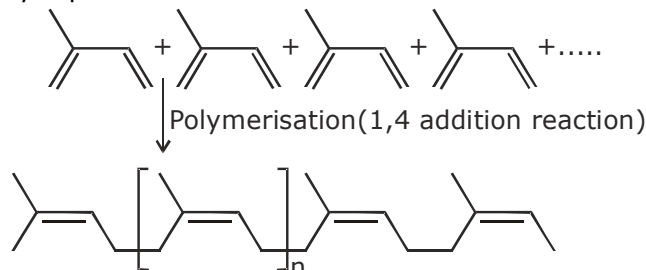
#### **1. Natural Rubber**

Natural rubber is obtained from nearly five hundred different plants but the main source is a braziliensis

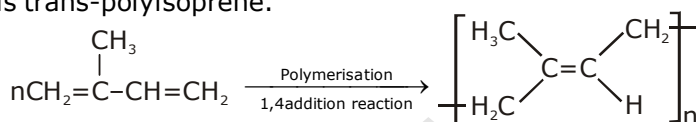


tree. It is obtained in the form of milky sap known as latex. This latex is coagulated with acetic acid and formic acid. The coagulated mass is then squeezed.

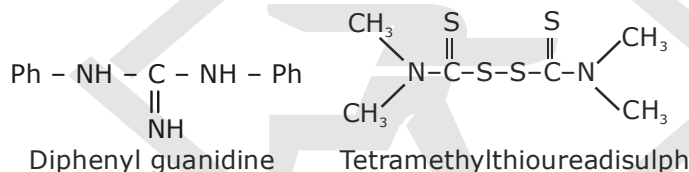
The raw natural rubber is a soft gummy and sticky mass. It is insoluble in water, dilute acids and alkalies but soluble in non-polar solvents. It has low elasticity and low tensile strength. Natural rubber is a polymer of 2-methyl-1, 3-butadiene (isoprene). On average, a molecule of rubber contains 5000 isoprene units held together by head to tail. All the double bonds in rubber are cis, hence natural rubber is cis-polyisoprene.



Gutta - percha is a naturally occurring isomer of rubber in which all the double bonds are trans. Thus, gutta-percha is trans-polyisoprene.



It is harder and more brittle than rubber. It is a filling material that dentists use in root canal treatment. In order to give strength and elasticity to natural rubber, it is vulcanized. Heating of rubber with sulphur or sulphur containing compound at 150°C for few hours is known as vulcanisation. The essential feature of the vulcanisation is the formation of cross-linking between the polymeric chains. This cross-linking gives mechanical strength to the rubber. Vulcanisation process can be enhanced in the presence of certain organic compounds known as accelerators. The common accelerators are:



In addition, fillers such as carbon black and zinc oxide are usually added to the crude rubber before vulcanisation in order to improve its wearing characteristics.

Natural rubber is used for making shoes, water - proof coats and golf balls. Vulcanised rubber is used for manufacture of rubber bands, gloves, tubing and car tyres.

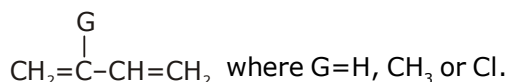
### SYNTHETIC RUBBER OR POLYMERISATION OF DIENES

Polymers of 1, 3 - butadienes are called synthetic rubbers because they have some of the properties of natural rubbers including the fact that they are water proof and elastic.

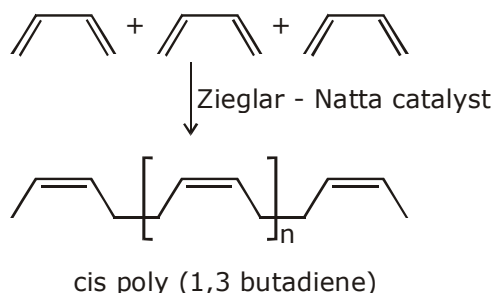
Synthetic rubbers have some improved properties. They are more flexible, tougher and more durable than natural rubber.

#### 1. Homopolymers

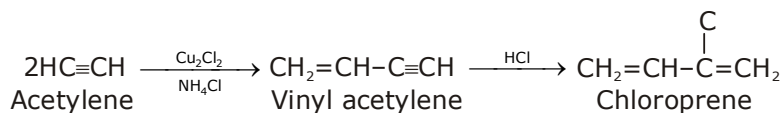
Monomer of this class is 2-substituted-1, 3-butadienes.



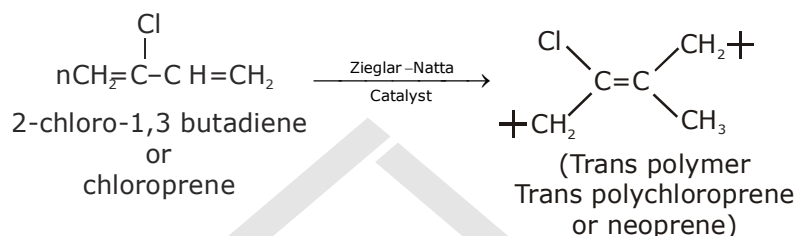
Polymerisation is always carried out in the presence of Ziegler-natta catalyst which gives stereoregular polymers.



Neoprene was the first synthetic rubber manufactured on large scale. It is also called dieprene. Its monomer, chloroprene (2-chlorobutadiene) is prepared from acetylene.



Chloroprene undergoes free radical polymerisation to form neoprene (polychloroprene).



Many of the properties of neoprene are similar to natural rubber but neoprene is more resistant to action of oils, gasoline and other hydrocarbons. It is also resistant to sunlight, oxygen, ozone and heat. It is non-inflammable.

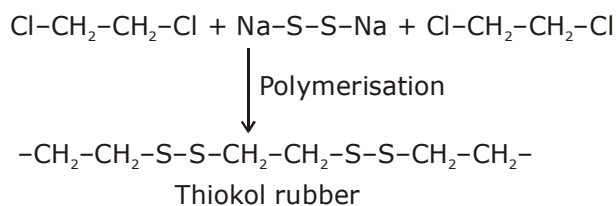
It is used for making automobile and refrigerator parts, hoses for petrol and oil containers, insulation of electric wires and conveyor belts.

## 2. Copolymers

The following synthetic rubbers are example of copolymers.

	Synthetic rubber	Monomers
1.	Buna-S, SBR (styrene-Butadiene rubber)	$\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ (25%) (75%)
2.	Buna-N, NBR (Nitrile-Butadiene rubber)	$\text{CH}_2=\text{CH}-\text{CN} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ (25%) (75%)
3.	Butyl rubber	$\text{CH}_3-\text{C}=\text{CH}_2 + \text{Butadiene}$ $\quad   \quad \quad \quad 2\%$ $\quad \text{CH}_3 \quad \quad \quad 98\%$
4.	ABS; Acrylonitrile, Butadiene, Styrene	$\text{CH}_2=\text{CH}-\text{CN} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ $\quad \quad \quad + \text{C}_6\text{H}_5\text{CH}=\text{CH}_2$

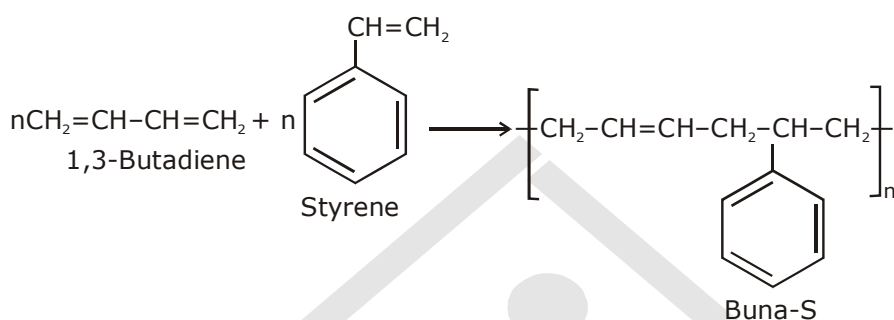
(a) **Thiokol** : Thiokol is made by polymerising ethylene chloride and sodium polysulphide.



The repeating unit is  $-\text{CH}_2-\text{S}-\text{S}-\text{CH}_2-$

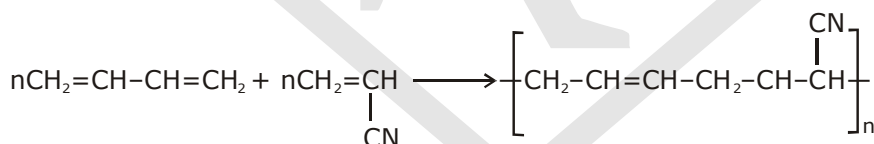
Thiokol is chemically resistant polymer. It is used in the manufacture of hoses and tank linings, engine gaskets and rocket fuel when mixed with oxidising agents.

- (b) Buna-S (SBR : Styrene-butadiene rubber) :** Buna-S rubber is a copolymer of three moles of butadiene and one mole of styrene. In buna-S, 'Bu' stands for butadiene, 'na' for symbol of sodium (Na) which is a polymerizing agent and 'S' stands for styrene. It is an elastomer (General purpose styrene Rubber or GRS).



Buna-S is generally compounded with carbon black and vulcanised with sulphur. It is extremely resistant to wear and tear therefore used in the manufacture of tyres and other mechanical rubber goods. It is obtained as a result of free radical copolymerisation of its monomers.

- (c) Buna-N :** It is obtained by copolymerisation of butadiene and acrylonitrile (General purpose Rubber acrylonitrile or GRA).



It is very rigid and is very resistant to action of petrol, lubricating oil and many organic solvents. It is mainly used for making fuel tanks.

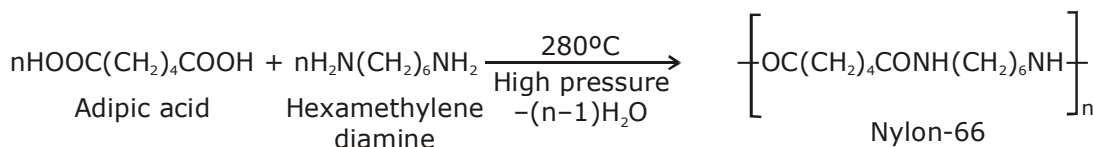
- (d) Cold Rubber :** Cold rubber is obtained by polymerization of butadiene and styrene at  $-18^{\circ}$  to  $5^{\circ}\text{C}$  temperature in the presence of redox system. Cold rubber has a greater tensile strength and greater resistance to abrasion than SBR.

## NYLON

Nylon is used as a general name for all synthetic fibres forming polyamides, i.e., having a protein like structure. A number is usually suffixed with the name 'nylon' which refers to the number of carbon atoms present in the monomers.

- (1) NYLON -66** (Nylon six, six)

It is obtained by the condensation polymerization of hexamethylenediamine (a diamine with six carbon atoms) and adipic acid (a dibasic acid having 6 carbon atoms).



**(2) NYON-6, 10** (Nylon six, ten)

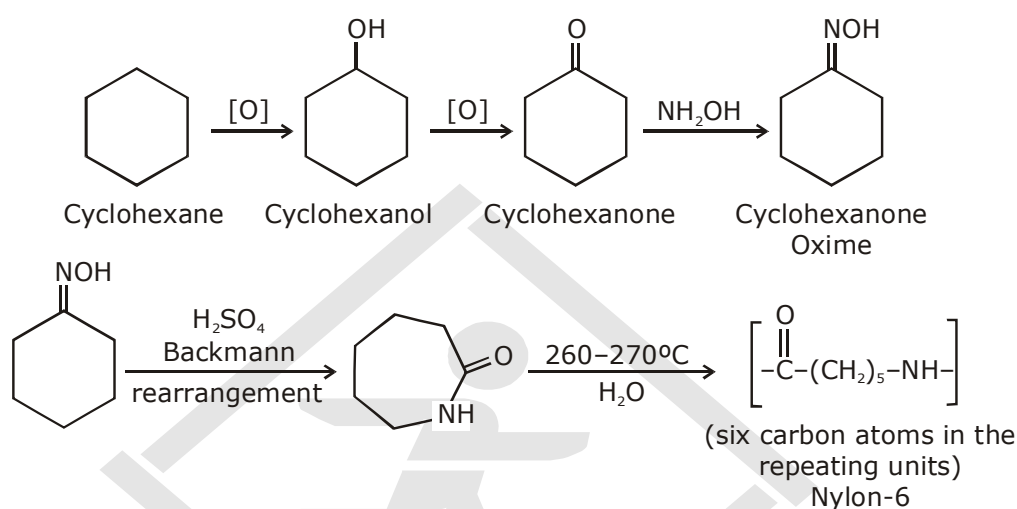
It is obtained by condensation polymerisation of hexamethylenediamine (six carbon atoms) and sebacic acid (a dibasic acid with 10 carbon atoms).

Nylon fibres are stronger than natural fibres and so are used in making cords and ropes. The fibres are elastic, light, very strong and flexible. They have drip dry property and retain creases. It is inert towards chemicals and biological agents. It can be blended with wool. Nylon fibres are used in making garments, carpets, fabrics, tyre cords, ropes etc.

**(3) NYON-6 (Perlon L)**

A polyamide closely related to nylon is known as perlon L (Germany) or Nylon-6 (USA). It is prepared by prolonged heating of caprolactam at 260°-270°C. It is formed by self condensation of a large number of molecules of amino caproic acid. Since, caprolactam is more easily available, it is used for polymerization, with is carried out in the presence of H<sub>2</sub>O that first hydrolyses the lactam to amino acid. Subsequently, the amino acid can react with the lactam and the process goes on and into form the polyamide polymer.

Caprolactam is obtained by Backmann rearrangement of cyclohexanone oxime.

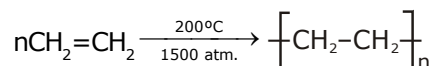
**(4) NYON-2 – NYLON-6**

It is an alternating polyamide copolymer of glycine and amino caproic acid and is biodegradable.

**POLYETHYLENE**

Polyethylene is of two types:

- (a) Low Density Poly Ethylene (LDPE) :** It is manufactured by heating ethylene at 200°C under a pressure of 1500 atmospheres and in the presence of traces of oxygen. This polymerisation is a free radical polymerisation.



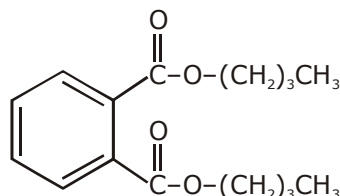
The polyethylene produced has a molecular mass of about 20,000 and has a branched structure. Due to this, polyethylene has a low density (0.92) and low melting point (110°C). That is why polyethylene prepared by free radical polymerisation is called low density polyethylene. It is a transparent polymer of moderate tensile strength and high toughness. It is widely used as a packing material and as insulation for electrical wires and cables.

- (b) High Density Poly Ethylene (HDPE) :** It is prepared by the use of Ziegler - Natta catalyst at 160°C under pressure of 6 to 7 atmospheres.

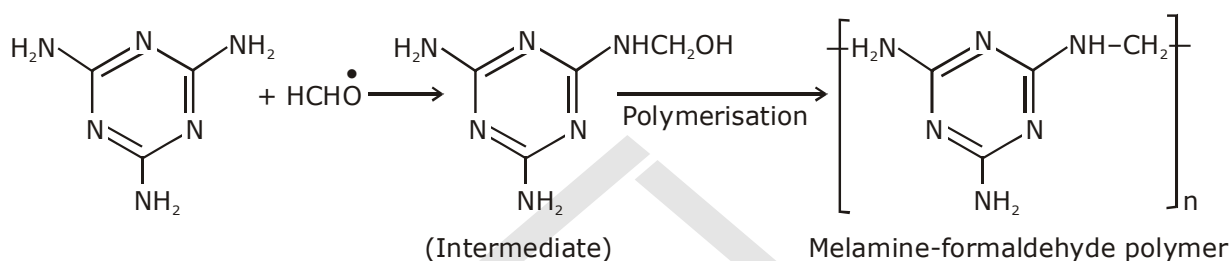
The polymer is linear chain, hence it has high density (0.97) and has high melting point (130°C). That is why it is called high density polyethylene. It is a translucent polymer. It has greater toughness, hardness and tensile strength than low density polyethylene. It is used in the manufacture of containers (buckets, tubes), house wares, bottles and toys.

**PLASTICISER**

A plasticiser is an organic compound that dissolves in the polymer and allows the polymer chains to slide past one another. This makes polymer more flexible. Dibutylphthalate is a commonly used plasticiser.

**MELAMINE - FORMALDEHYDE RESIN**

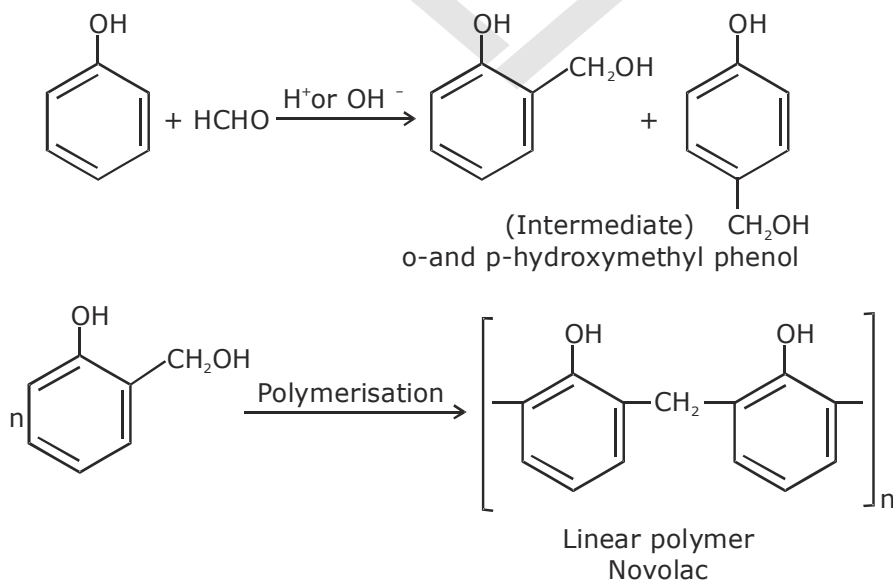
This resin is formed by condensation polymerisation of melamine and formaldehyde.

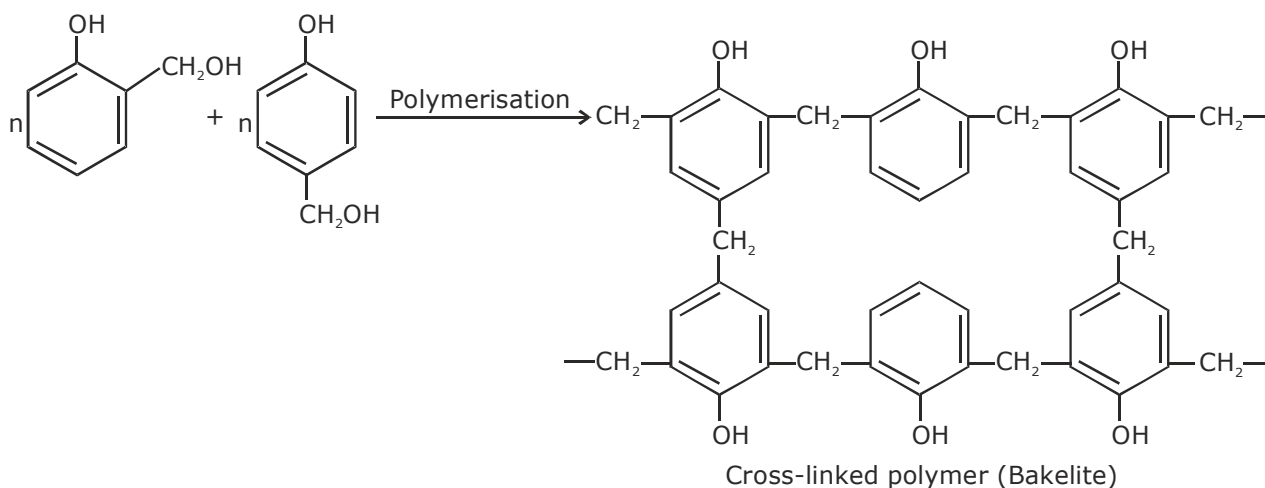


It is a quite hard polymer and is used widely for making plastic crockery under the name melamine. The articles made from this polymer do not break even when dropped from considerable height.

**BAKELITE**

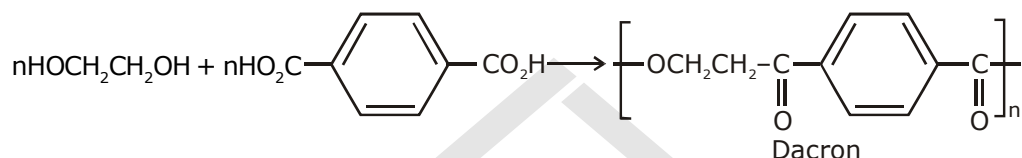
Phenol-formaldehyde resins are obtained by the reaction of phenol and formaldehyde in the presence of either an acid or a basic catalyst. The reaction starts with the initial formation of ortho and para-hydroxymethyl phenol derivatives, which further react with phenol to form compounds where rings are joined to each other with  $-CH_2-$  groups. The reaction involves the formation of methylene bridges in ortho, para or both ortho and para positions. Linear or cross-linked materials are obtained depending on the conditions of the reaction.





### POLYESTERS

Dacron is a common polyester, prepared using ethylene glycol and terephthalic acid. The reaction is carried out at  $140^\circ$  to  $180^\circ$  C in the presence of zinc acetate and  $\text{Sb}_2\text{O}_3$  as catalyst.



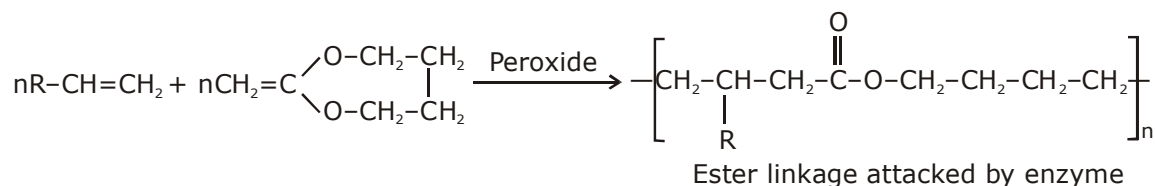
The terylene fibre (Dacron) is crease resistant and has low moisture absorption. It has high tensile strength. It is mainly used in making wash and wear garments, in blending with wool to provide better crease and wrinkle resistance.

### BIODEGRADABLE POLYMERS

By far the largest use of synthetic polymers is as plastic. A major portion of it is used as throwaway containers and packing materials. Since plastics do not disintegrate by themselves, they are not biodegradable over a period of time. Non-biodegradability is due to the carbon-carbon bonds of addition polymers which are inert to enzyme catalysed reaction. These polymers create pollution problem.

Biodegradable polymers are the polymers that can be broken into small segments by enzyme catalysed reactions using enzymes produced by microorganisms. In biodegradable polymers, bonds that can be broken by the enzymes are inserted into the polymers. Therefore, when they are buried as waste, enzymes present in the ground can degrade the polymer.

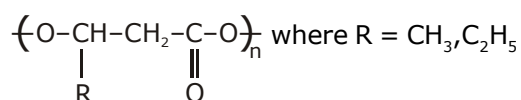
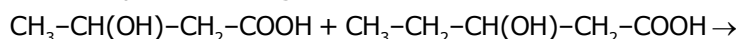
One method involves inserting hydrolysable ester group into the polymer. For example, when acetal (I) is added during the polymerization of alkene, ester group is inserted into the polymeric chains.



Aliphatic polyesters are important class of biodegradable polymers. Some examples are described below:

**(1) Poly - Hydroxybutyrate-CO-β-Hydroxyvalerate (PHBV)**

It is a copolymer of 3-hydroxybutanoic acid and 3 hydroxypentanoic acid, in which the monomer units are connected by ester linkages.



The properties of PHBV vary according to the ratio of both the acids. 3-Hydroxybutanoic acid provides stiffness and 3-hydroxypentanoic acid imparts flexibility to the co-polymer. It is used in specialty packaging, orthopaedic devices and even in controlled drug release. When a drug is put in a capsule of PHBV. It is released only after the polymer is degraded. PHBV also undergoes bacterial degradation in the environment.

**(2) POLY (GLYCOLIC ACID) AND POLY (LACTIC ACID)**

They constitute commercially successful biodegradable polymers such as sutures. Dextron was the first bioadsorbable suture made for biodegradable polyesters for post - operative stitches.

**MOLECULAR MASS OF POLYMER**

Normally, a polymer contains chains of varying lengths and therefore, its molecular mass is always expressed as an average. In contrast, natural polymers such as protein contains chain of identical length and hence, have definite molecular mass.

The molecular mass of a polymer is expressed as

- (a) Number average molecular mass ( $\bar{M}_n$ )

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

Where  $N_i$  is the number of molecules of molecular mass  $M_i$

- (b) Weight average molecular mass ( $\bar{M}_w$ )

$$\bar{M}_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

Where  $N_i$  is the number of molecules of molecular mass  $M_i$ . Methods such as light scattering and ultracentrifuge depend on the mass of individual molecules and yield weight average molecular masses.

$\bar{M}_n$  is determined by employing methods which depend upon the number of molecules present in the polymer sample viz. Colligative properties like osmotic pressure.

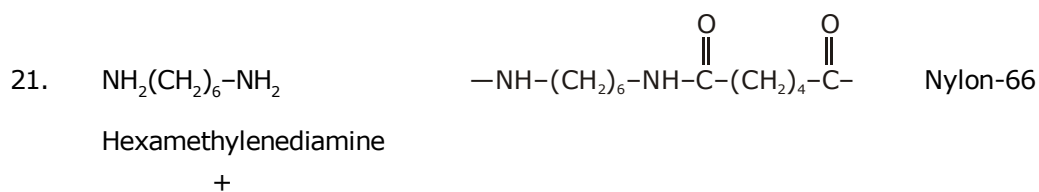
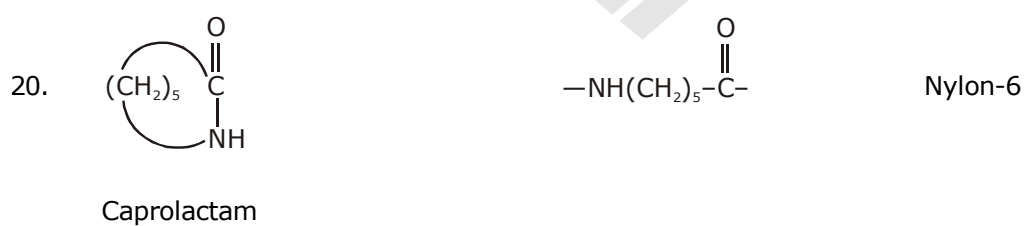
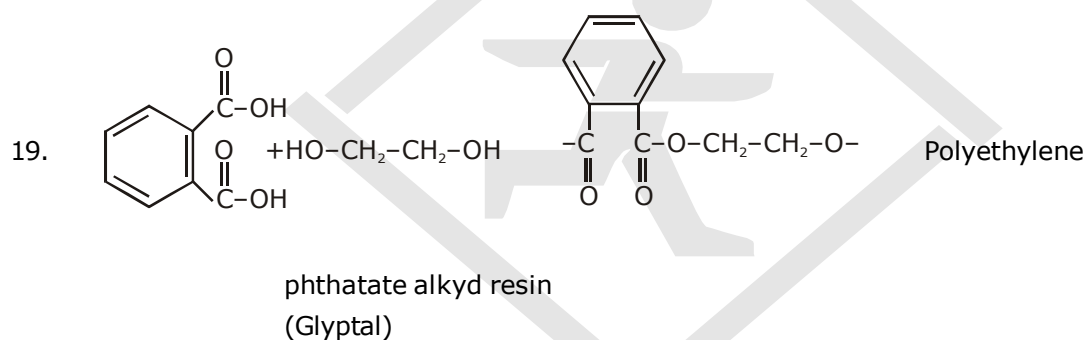
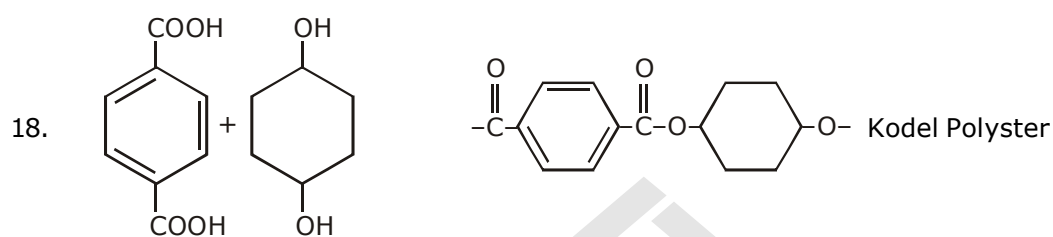
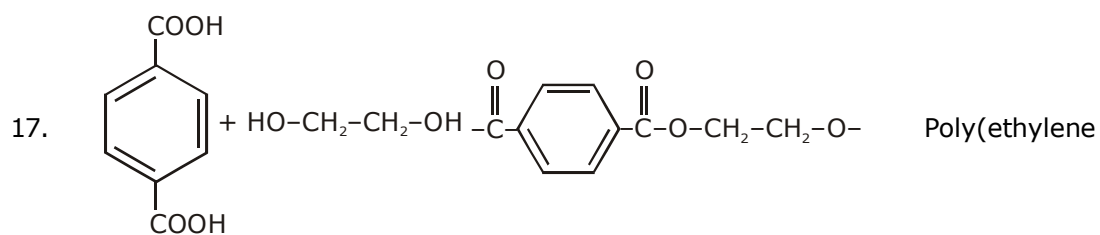
The ratio of the weight and number average molecular masses ( $\bar{M}_w/\bar{M}_n$ ) is called Poly Dispersity Index (PDI). Some natural polymers, which are generally monodispersed, the PDI is unity (i.e.  $\bar{M}_w = \bar{M}_n$ ). In synthetic polymers, which are always polydispersed,  $\text{PDI} > 1$  because is always higher than  $\bar{M}_n$ .

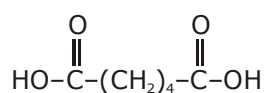
### COMMON POLYMERS

Monomer	Repeating unit	Polymer
1. $\text{CH}_2=\text{CH}_2$ Ethylene	$-\text{CH}_2-\text{CH}_2-$	Polyethylene
2. $\text{CH}_3-\text{CH}=\text{CH}_2$ Propene	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{CH}_2-\text{CH}_2- \end{array}$	Polypropene
3. $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$ Styrene	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\   \\ \text{C}_6\text{H}_5 \end{array}$	Polystyrene
4. $\text{CF}_2=\text{CF}_2$ Tetrafluoroethylene	$-\text{CF}_2-\text{CF}_2-$ ethylene (PTFE), Teflon	Polytetrafluoro
5. $\text{CH}_2=\text{CH}-\text{Cl}$ Vinyl chloride	$\begin{array}{c} \text{Cl} \\   \\ -\text{CH}_2-\text{CH}- \end{array}$	Polyvinyl Chloride (PVC)
6. $\text{CH}_2=\text{CH}-\text{CN}$ Vinyl cyanide or	$\begin{array}{c} \text{CN} \\   \\ -\text{CH}_2-\text{CH}- \end{array}$ poly acrylonitrile,	Polyvinyl cyanide, Acrylonitrile Orlon.
7. $\begin{array}{c} \text{H}_3\text{C} \quad \text{O} \\   \quad    \\ \text{CH}_2=\text{C}-\text{C}-\text{O}-\text{CH}_3 \end{array}$ Methyl methacrylate	$\begin{array}{c} \text{COOCH}_3 \\   \\ -\text{CH}_2-\text{C}- \\   \\ \text{CH}_3 \end{array}$ Plexiglas, Lucite	Polymethyl metha acrylate,

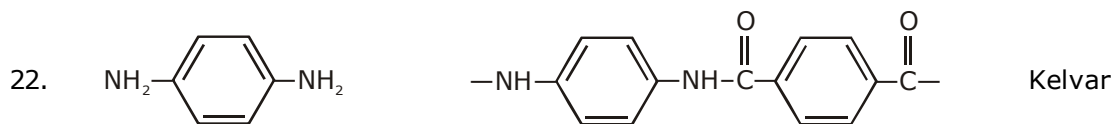


8.  $\text{CH}_2=\text{CH}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$   $-\text{CH}_2-\overset{\text{OCOCH}_3}{\underset{|}{\text{CH}}}-$  Polyvinyl Acetate  
Vinyl acetate
9.  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$   $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$  Polybutadiene,  
1, 3-butadiene Buna rubber
10.  $\text{CH}_2=\text{CH}-\text{Cl}$  (vinyl chloride)  $-\text{CH}_2-\overset{\text{Cl}}{\underset{|}{\text{CH}}}-\text{CCl}_2-\text{CH}_2-$  Saran  
+  
 $\text{CH}_2=\text{CCl}_2$  (Vinylidene chloride)
11.  $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$  (Styrene)  $-\text{CH}_2-\overset{\text{C}_6\text{H}_5}{\underset{|}{\text{CH}}}-\overset{\text{CN}}{\underset{|}{\text{CH}}}-\text{CH}_2-$  SAN  
+  
 $\text{CH}_2=\text{CH}-\text{CN}$  (acrylonitrile)
12.  $\text{CH}_2=\text{CH}-\text{CN} + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$  - ABS  
+  
 $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$
13.  $\text{CH}_2=\overset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{CH}_2 + \text{CH}_2=\overset{\text{CH}_3}{\underset{|}{\text{C}}}-\text{CH}=\text{CH}_2$  - Butyl rubber  
 $\text{CH}_3$
14.  $\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2 + \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$  - Buna-S, SBR
15.  $\text{CH}_2=\text{CH}-\text{CN} + \text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$  - Buna-N, NBR
16.  $\text{CH}_2=\overset{\text{Cl}}{\underset{|}{\text{C}}}-\text{CH}=\text{CH}_2$   $-\text{CH}_2-\overset{\text{Cl}}{\underset{|}{\text{C}}}=\text{CH}-\text{CH}_2-$  Neoprene  
Chloroprene



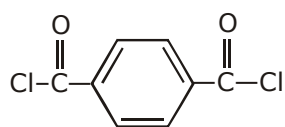


Adipic Acid

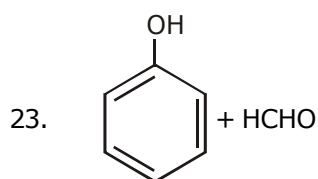


1, 4-Diaminobenzene

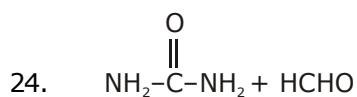
+



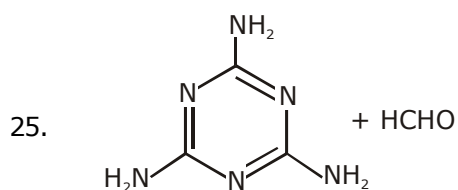
Terephthaloyl chloride



– Bakelite or resol



– Urea-formaldehyde resin



– Melamine-

Malamine

formaldehyde resin

**PRACICAL ORGANIC CHEMISTRY****(A) FUNCTIONAL GROUP ANALYSIS****1. Unsaturation : Alkenes & alkynes :**

- (a) Bayers test : Cold dil alk.  $\text{KMnO}_4$  decolourisation test  
Purple colour Colourless +  $\text{MnO}_2$  (Brown ppt)
- (b)  $\text{Br}_2$  water decolourisation test  
Violet colourless of  $\text{Br}_2 \rightarrow$  Colourless

**2. Terminal alkynes :**

Confirmed by ppt of Acetylide ion with  $\text{NaNH}_2$  or  $\text{AgNO}_2$  or  $\text{Cu}_2\text{Cl}_2\text{NH}_4\text{OH}$

**3. Alkyl halides :**

- (a) If they are capable of carbocation formation then they will give ppt with  $\text{AgNO}_3$ .
- (b) Beilstein's test : A green colour is imported to the flame if small amount of organic compound is taken on copper wire.

**4. Alcohol :**

- (a) Cerric ammonium nitrate  $\rightarrow$  Give red colour
- (b) Boil with acetic acid & conc.  $\text{H}_2\text{SO}_4 \rightarrow$  fruity smell
- (c) 2-alkanol & ethanol also give Iodoform test  $\rightarrow$  Yellow ppt. of  $\text{CH}_3\text{I}$  on reaction with  $\text{I}_2 + \text{OH}^\ominus$

**5. Aldehyde & ketones :**

2,4-Dinitrophenyl hydrazine (or) Braddy's reagent give yellow, orange or red colour with ald. & Ketones (2, 4-DNP)

**6. Aldehydes :**

- (a) Tollen's test  $\rightarrow$  Silver mirror
- (b) Fehling's test {except benzaldehyde}  $\rightarrow$  Red colour
- (c) Benedicts test  $\rightarrow$  Red colour
- (d) Schiff's dye colour regeneration test  $\rightarrow$  Pink colour
- (e) Gly ppt. with  $\text{HgCl}_2$ .

**7. Ketones :**

- (a) methyl ketones give haloform test
- (b)  $\alpha$ -hydroxy Ketones give Tollen's & Fehling test's too.

**8. Carboxylic acids :**

- (a) Brisk effervescence with aq.  $\text{NaHCO}_3$  solution.
- (b)  $\text{HCOOH}$  alone gives silver mirror test with Tollen's reagent.
- (c) Blue litmus  $\rightarrow$  red
- (d) give fruity smell of reaction with alcohols.

**9. Phenols :**

- (a) Violet colouration with neutral  $\text{FeCl}_3$
- (b) Liebermann test
- (c) White ppt. with  $\text{Br}_2$  water
- (d) Brisk effervescence with aq.  $\text{NaHCO}_3$  is observed in case of Nitrophenols.

**10. Primary amines :**

- (a) Carbylamine reaction  $\rightarrow$  Isonitriles have very distinctive foul odors
- (b) Hoffmann mustard oil reaction  $\rightarrow$  Oily liquid with mustard like smell.

**11. Aromatic  $1^\circ$  amine  $\rightarrow$  diazo test****12. Amide boil with  $\text{NaOH} \rightarrow \text{NH}_3$** **13. Nitrobenzene  $\rightarrow$  Mulliken Baker test  $\rightarrow$  Treat it with  $\text{ZnNH}_4\text{Cl}$  then boil with Tollen's reagent  $\rightarrow$  Silver mirror will appear****14. Proteins :**

- (a) Biuret test : Also used for urea  $\rightarrow$  Alkaline solution of protein treated with a drop of aq  $\text{CuSO}_4$  when bluish violet colour is obtained
- (b) Ninhydrin test: Protein treated with a puridine solution of ninhydrin give colour ranging from deep blue to violet pink.

**DIFFERENTIATION TEST****D1.  $1^\circ$ ,  $2^\circ$  &  $3^\circ$  alcohols :**

- (a) Luca's test : Lucas reagent is conc.  $\text{HCl} + \text{ZnCl}_2$
- (b) Victor Meyer's test (RBC test)
  - (i)  $1^\circ$  Alcohol  $\rightarrow$  Blood red colour
  - (ii)  $2^\circ$  Alcohol  $\rightarrow$  Blue
  - (iii)  $3^\circ$  Alcohol  $\rightarrow$  Colourless

**D2.  $1^\circ$ ,  $2^\circ$  &  $3^\circ$  amines :**

- (a) Hinsberg's reagent
  - (i)  $1^\circ$  Amine yield a clear solution from which upon acidification an insoluble material separated.
  - (ii)  $2^\circ$  Amine yield an insoluble compound which is unaffected by acid
  - (iii)  $3^\circ$  Amine yield insoluble compound
- (b) Reaction with  $\text{HNO}_2$ .

1. Natural rubber is a polymer of  
(1) Chloroprene (2) Isoprene  
(3) 1,3-Butadiene (2) None
2. Hydrolysis of sucrose is called  
(1) saponification (2) Inversion  
(3) Esterification (2) Hydration
3. In vulcanization of rubber  
(1) Sulphur reacts to form a new compound  
(2) Sulphur cross-links are introduced  
(3) Sulphur forms a very thin protective layer over rubber.  
(2) All statements are correct.
4. Which of the following belong to the class of natural polymers ?  
(1) Proteins (2) Cellulose  
(3) Rubber (4) All of the above
5. The reaction of glucose and red P + HI is called  
(1) Sandmeyer's reaction (2) Reformatsky reaction  
(3) Gattermann's reaction (4) Reduction
6. The reagent used in Ruff degradation is :  
(1) baeyer's reagent (2) Tollen's reagent  
(3) Fenton's reagent (4) Benedict's reagent
7. Number of possible isomers of glucose is:  
(1) 10 (2) 14  
(3) 16 (4) 20
8. Glucose reacts with acetic anhydride to form  
(1) Monoacetate (2) Tetra acetate  
(3) Penta acetate (4) Hexa acetate
9. Glucose or aldohexose contains  
(1) ONE -CHO group  
(2) Five -OH groups  
(3) One primary alcoholic group and four secondary alcoholic groups  
(4) All are correct
10. When glucose is heated with nitric acid, the product is  
(1) Gluconic acid (2) Glucaric acid  
(3) Glycolic acid (4) Oxalic acid
11. Cane sugar is made of  
(1) 5 membered glucose ring and 5 membered fructose ring  
(2) 6 membered glucose ring and 6 membered fructose ring  
(3) 6 membered glucose ring and 5 membered fructose ring  
(4) 6 membered galactose ring and 6 membered fructose ring

**(A) ELEMENTAL ANALYSIS****Lassaigne Method (Detection of Elements)**

Element	Sodium Extract (S.E.)	Confirmed Test	Reactions
Nitrogen	$\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN(S.E.)}$	S.E. + $\text{FeSO}_4 + \text{NaOH}$ , boil and cool, + $\text{FeCl}_3 + \text{conc. HCl}$ Blue or green colour (i) S.E. + sodium nitro prusside (A) A deep violet colour	$\text{FeSO}_4 + 2\text{NaOH} \longrightarrow \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4$ $\text{Fe(OH)}_2 + 6\text{NaOH} \longrightarrow \text{Na}_4[\text{Fe(CN)}_6] + 2\text{NaOH}$ $\text{Na}_4[\text{Fe(CN)}_6] + \text{FeCl}_3 \xrightarrow{\text{HCl}} \text{Fe}_4[\text{Fe(CN)}_6]_3 + 3\text{NaCl}$ Prussian blue (i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe(CN)}_5\text{NO}] \longrightarrow \text{Na}_4[\text{Fe(CN)}_5\text{NOS}]$ (A) deep violet (ii) $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}} \text{PbS} \downarrow + 2\text{CH}_3\text{COONa}$ black ppt.
Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S(S.E.)}$	(ii) S.E. + $\text{CH}_3\text{COOH}$ + $(\text{CH}_3\text{COO})_2\text{Pb}$ A black ppt. S.E. + $\text{HNO}_3 + \text{AgNO}_3$ (i) White ppt. soluble in aq. $\text{NH}_3$ confirms Cl (ii) Yellow ppt.	
Halogen	$\text{Na} + \text{Cl} \xrightarrow{\Delta} \text{NaCl(S.E.)}$	partially soluble in aq. $\text{NH}_3$ confirm Br (iii) Yellow ppt. in soluble in aq. $\text{NH}_3$ confirms I As in test for nitrogen; instead of green or blue colour, blood red colouration confirms presence of N and S both	$\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow$ ppt. $\text{AgCl} + 2\text{NH}_3(\text{aq}) \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$ white ppt. soluble $\text{NaCNS} + \text{FeCl}_3 \longrightarrow [\text{Fe(CNS)}]\text{Cl}_2 + \text{NaCl}$ blood red colour
Nitrogen and Sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaCNS(S.E.)}$		

**EXERCISE – I****OBJECTIVE PROBLEMS (JEE MAIN)**

**1.** Which of the following monosaccharides is a pentose-

- (A) Glucose (B) Fructose  
(C) Ribose (D) Galactose

**Sol.**

**Q.2** Ring structure of glucose is due to formation of hemiacetal and ring formation between-

- (A) C<sub>1</sub> and C<sub>5</sub> (B) C<sub>1</sub> and C<sub>4</sub>  
(C) C<sub>1</sub> and C<sub>3</sub> (D) C<sub>2</sub> and C<sub>4</sub>

**Sol.**

**Q.3** Glucose is-

- (A) Monosaccharide (B) Disaccharide  
(C) Trisaccharide (D) Polysaccharide

**Sol.**

**Q.4** Hydrolysis of sucrose is called-

- (A) Esterification (B) Saponification  
(C) Inversion (D) Hydration

**Sol.**

**Q.5** Starch is changed into disaccharide in presence of-

- (A) Amylase (B) Maltase  
(C) Lactase (D) Zymase

**Sol.**

**Q.6** The disaccharide present in milk is-

- (A) Sucrose (B) Maltose  
(C) Lactose (D) Cellobiose

**Sol.**

**Q.7** The pH value of the solution in which a particular amino acid does not migrate under the influence of electric field is called its-

- (A) Eutectic point  
(B) Neutralisation point  
(C) Isoelectric point  
(D) Effusion point

**Sol.**

**Q.8** The number of essential amino acids for the growth & maintenance of life is-

- (A) 1 (B) 2  
(C) 4 (D) 8

**Sol.**

**Q.9** Secondary structure of proteins refers to-

- (A) Mainly denatured proteins and structure of prosthetic group  
(B) Three dimensional structure specially the bond between amino acid residues that are distant from each other in polypeptide chain  
(C) Linear sequence of amino acid residue in the polypeptide chain  
(D) Regular folding patterns of continuous portion of the polypeptide chain

**Sol.**

**Q.10** A pigment protein in animals is-

- (A) Chlorophyll (B) Insulin  
(C) Keratin (D) Haemoglobin

**Sol.**

**Q.11** The main structural feature of proteins is-

- (A) An ester linkage  
(B) An ether linkage  
(C) The peptide linkage (D) All



**Sol.**

- Q.12**  $\alpha$ -Helical structure refers to the-  
(A) Primary structure of protein  
(B) Secondary structure of protein  
(C) Tertiary structure of protein  
(D) Quaternary structure of proteins

**Sol.**

- Q.13** Simplest amino acid is-  
(A) Lysine (B) Glycine  
(C) Leucine (D) Alanine

**Sol.**

- Q.14** 'Kwashiorkor' is a disease caused by the deficiency of-  
(A) Vitamins (B) Hormones  
(C) Blood (D) Essential amino acids

**Sol.**

- Q.15** Hair, finger, nails, hoofs etc. are all made of-  
(A) Fat (B) Vitamins  
(C) Proteins (D) Iron

**Sol.**

- Q.16** Mark the globular protein in the following-  
(A) Collagen  
(B) Myoglobin or Haemoglobin  
(C) Myosin (D) Fibroin

**Sol.**

- Q.17** The end product of protein digestion is-  
(A) Peptides (B) Peptones  
(C) Protines (D)  $\alpha$ -Amino acids

**Sol.**

- Q.18** The enzyme pepsin hydrolyses-  
(A) Proteins to peptides  
(B) Fats to fatty acids  
(C) Glucose to ethyl alcohol  
(D) Polysaccharides to monosaccharides

**Sol.**

- Q.19** Which one is the complimentary base of adenine in one strand to that in the other strand of DNA-  
(A) Cytosine (B) Guanine  
(C) Uracil (D) Thymine

**Sol.**

- Q.20** The base present in RNA but not found in DNA is-  
(A) Thymine (B) Uracil  
(C) Adenine (D) Guanine

**Sol.**

- Q.21** Calorific value is in the order-  
(A) Fats > Proteins > Carbohydrates  
(B) Carbohydrates > Fats > Protein  
(C) Fats > Carbohydrates > Protein  
(D) Protein > Fats > Carbohydrates

**Sol.**

- Q.22** Ptyalin of saliva acts in:  
(A) Slightly acidic medium  
(B) Slightly alkaline medium  
(C) Neutral medium  
(D) All types of medium

**Sol.**

- Q.23** Deficiency of vitamin A results in:  
(A) Scurvy (B) Night blindness  
(C) Beri-beri (D) Rickets

**Sol.**

**Q.24** Riboflavin deficiency causes-  
(A) Scurvy (B) Pellagra  
(C) Beri-beri (D) Cheilosis

**Sol.**

**Q.25** Sunshine vitamin is:  
(A) E (B) C (C) D (D) A

**Sol.**

**Q.26** A good source of vitamins A and D is:  
(A) Whole cereal (B) Cod liver oil  
(C) Yeast (D) Water melon

**Sol.**

**Q.27** Vitamin B takes part in :  
(A) increase in blood pressure  
(B) decrease in blood pressure  
(C) activating bone marrow  
(D) maturation of RBC's

**Sol.**

**Q.28** Ascorbic acid is called as:  
(A) Vit. C (B) Vit. A  
(C) Vit. D (D) Vit. B

**Sol.**

**Q.29** Cyanocobalamin is the chemical name of:  
(A) Vitamin B1 (B) Vitamin B2  
(C) Vitamin B6 (D) Vitamin B12

**Sol.**

**Q.30** Continuous bleeding from an injured part of body is due to deficiency of:  
(A) Vitamin A (B) Vitamin E  
(C) Vitamin B (D) Vitamin K

**Sol.**

**Q.31** Milk protein is-  
(A) Lactose (B) Myosin  
(C) Casein (D) Pepsin

**Sol.**

**Q.32** Cobalt as a rare element is essential in the synthesis of this vitamin:  
(A) Vitamin C (B) Vitamin D  
(C) Vitamin B<sub>1</sub> (D) Vitamin B<sub>12</sub>

**Sol.**

**Q.33** Which of the following is an essential amino acid?  
(A) Serine (B) Cysteine  
(C) Glycine (D) Phenylalanine

**Sol.**

**Q.34** Vitamin necessary for blood clotting is:  
(A) E (B) C  
(C) K (D) D

**Sol.**

**Q.35** Scurvy is a disease caused by:  
(A) a virus  
(B) deficiency of vitamin E  
(C) deficiency of ascorbic acid  
(D) deficiency of vitamin D

**Sol.**

**Q.36** Which pairing is found in DNA-  
(A) Adenine with thymine  
(B) Thymine with guanine  
(C) Guanine with adenine  
(D) Uracil with adenine

**Sol.**

**Q.37** The acidic characters of DNA and RNA are due to:  
(A) purine bases (B) sugar molecules  
(C) pyrimidine bases (D) phosphoric group

**Sol.**

- Q.38** According to the Chargaff's law:  
(A)  $A + T = G + C$  (B)  $T + A = C$   
(C)  $A + T + G = C$  (D)  $\frac{A+G}{C+T} = 1$

**Sol.**

- Q.39** Those amino acids which can not be synthesised by animal bodies are called-  
(A) Non - essential (B) Essential  
(C) Energy yielding (D) Active

**Sol.**

- Q.40** DNA molecule is formed of-  
(A) Pentose sugar, pyrimidines and purines  
(B) Pentose sugar: Phosphoric acid, pyrimidines and purines  
(C) Pentose sugar, phosphoric acid, and purines  
(D) Chloridepentose sugar, phosphoric acid and pyrimidines,

**Sol.**

- Q.41** In DNA if 10% of guanine is present, how much thymine is present?  
(A) 10% (B) 20%  
(C) 40% (D) 80%

**Sol.**

- Q.42** In mammals carbohydrates are stored in the form of-  
(A) Lactic acid in muscles  
(B) Glycogen in liver and muscles  
(C) Glucose in liver and spleen  
(D) Glycogen in liver and spleen

**Sol.**

- Q.43** Which of the following is not a reducing sugar-  
(A) Sucrose (B) Galactose  
(C) Glucose (D) Lactose

**Sol.**

- Q.44** The sulphur containing essential amino acids bonded together in long peptide chains form-  
(A) Hydrocarbons (B) Nucleic acids  
(C) Organic acids (D) Proteins

**Sol.**

- Q.45** Find out the example of phosphoprotein-  
(A) Plasma membrane (B) Casein of milk  
(C) Haemoglobin (D) Mucin of saliva

**Sol.**

- Q.46** If a portion of DNA code is CAT, the anticodon for this code on t RNA will be-  
(A) GUA (B) GTA  
(C) ATG (D) AUG

**Sol.**

- Q.47** How many carbon atoms can be found in a monosaccharide-  
(A) 5-6 (B) 3-5  
(C) 3-7 (D) 1-5

**Sol.**

- Q.48** The nucleotides of one polynucleotide chain are joined together by-  
(A) Weak hydrogen bonds  
(B) Disulphide bonds  
(C) Phospho-diester bonds  
(D) Glycosidic bonds

**Sol.**

- Q.49** If 30% of an organism's DNA is thymine, then:  
 (A) 70% is purine (B) 20% is guanine  
 (C) 30% is adenine  
 (D) Both (B) and (C) are correct

**Sol.**

- Q.50** Deoxyadenylic acid, deoxyguanylic acid, deoxythymidylic acid & deoxycytidylic acid are-  
 (A) Nucleotides of DNA  
 (B) Fatty acids  
 (C) Nucleosides of DNA  
 (D) Nucleotides of RNA

**Sol.**

- Q.51** Which of the following substances is involved in all energy transformation reactions in a living system-  
 (A) Calcium (B) Phosphate  
 (C) Cyclic AMP (D) Creatinephosphate

**Sol.**

- Q.52** The base sequence for a nucleic acid segments is given as GAG, AGG, GGA, CGA, & CCA, from this it can be definitely concluded that it is a segment of-  
 (A) t-RNA (B) m-RNA  
 (C) DNA (D) Data not sufficient

**Sol.**

- Q.53** Nucleic acids are made of:  
 (A) Proteins (B) nucleotides  
 (C) amino acids (D) nucleosides

**Sol.**

- Q.54** A nucleoside is:  
 (A) base + sugar  
 (B) base + phosphate  
 (C) sugar + phosphate  
 (D) base + sugar + phosphate

**Sol.**

- Q.55** Characters are transferred from parents to offspring through-  
 (A) RNA (B) DNA  
 (C) Lipid (D) Protein

**Sol.**

- Q.56** Which of the following groups includes all essential amino acids for man-  
 (A) Leucine, methionine, lysine & valine  
 (B) Tryptophan, phenylalanine, glycine & glutamine  
 (C) Glutamine, valine & arginine  
 (D) Phenylalanine, valine, lysine, glycine tyrosine

**Sol.**

- Q.57** Base is not found in DNA is-  
 (A) Uracil (B) Adenine  
 (C) Guanine (D) Cytosine

**Sol.**

- Q.58** The similarity between DNA & RNA is that both-  
 (A) Are polymers of nucleotides  
 (B) Are always double stranded  
 (C) Have similar kind of sugar  
 (D) Have similar type of pyrimidine bases

**Sol.**

- Q.59** Semi conservative method of DNA duplication means-  
 (A) Newly synthesized DNA is conserved only in one cell cycle  
 (B) Newly synthesized DNA molecules have one strand from the parent DNA molecule  
 (C) Replication of DNA results in the formation of only one stranded daughter DNA  
 (D) Only one strand of DNA molecule form RNA

**Sol.**

- Q.60** In DNA, guanine pairs with:  
(A) Cytosine (B) Thymine  
(C) Adenine (D) Uracil

**Sol.**

- Q.61** Which of the following is not a copolymer-  
(A) Plexiglass (B) Buna-S  
(C) Nylon-66 (D) Dacron

**Sol.**

- Q.62** Polymerisation in which two or more chemically different monomers take part is called-  
(A) Addition polymerisation  
(B) Copolymerisation  
(C) Chain polymerisation  
(D) Homopolymerisation

**Sol.**

- Q.63** Chemical name of melamine is-  
(A) 2,4-Diamino-1,3,5-triazine  
(B) 2-Amino-1,3,5-triazine  
(C) 2,4,6 -Triamino-1,3,5-triazine  
(D) 1,3,5-Triamino-2,4,6-triazine

**Sol.**

- Q.64** Carpolactum is used to prepare which of the polymer-  
(A) Nylon – 66 (B) Melamine  
(C) Nylon – 6 (D) PMMA

**Sol.**

- Q.65** The fibre obtained by the condensation of hexamethylene diamine and adipic acid is-  
(A) Dacron (B) Nylon 66  
(C) Rayon (D) Teflon

**Sol.**

- Q.66** Of the following which is a step growth polymer-  
(A) Bakelite (B) Polyethylene  
(C) Teflon (D) PVC

**Sol.**

- Q.67** Bekelite is-  
(A) Addition polymer (B) Elastomer  
(C) Thermoplastic (D) Thermosett

**Sol.**

- Q.68** Perlon is-  
(A) Rubber (B) Nylon  
(C) Terylene (D) Orlon

**Sol.**

- Q.69** Nylon-6, 6 is made by the polycondensation of-  
(A) Adipic acid + Hexamethylene diamine  
(B) Phthalic acid + Glycerol  
(C) Phenol + Formaldehyde  
(D) Urea + Formaldehyde

**Sol.**

- Q.70** An example of a natural biopolymer is-  
 (A) Teflon (B) Neoprene  
 (C) Nylon-66 (D) DNA

**Sol.**

- Q.71** Natural silk is a-  
 (A) Polypeptide (B) Polyacrylate  
 (C) Polyester (D) Polysaccharide

**Sol.**

- Q.72** Peptide bond is a key feature in-  
 (A) Polysaccharide (B) Proteins  
 (C) Nucleotide (D) Vitamins

**Sol.**

- Q.73** Neoprene rubber is obtained by the polymerization of -  
 (A) 1, 3-Butadiene  
 (B) 2- Methyl -1, 3-butadiene  
 (C) 2- Chloro -1, 3 butadiene  
 (D) Styrene and butadiene

**Sol.**

- Q.74** Which of the following is not a natural polymer-  
 (A) Starch (B) Cellulose  
 (C) Glyptal (D) Glycogen

**Sol.**

- Q.75** Which of the following is natural polymer-  
 (A) Polyisoprene  
 (B) Polybutadiene  
 (C) Polyethylene terephthalate  
 (D) Polyethylene

**Sol.**

- Q.76** The example of thermosetting plastic and thermoplastic polymer respectively is-  
 (A) Polystyrene, polyvinyl chloride  
 (B) Bakelite, polystyrene  
 (C) Polythene, polyacrylonitrile  
 (D) Polystyrene, urea formaldehyde resin

**Sol.**

- Q.77** Which of the following is wrong-  
 (A) PMMA is called plexiglass  
 (B) PTFE is called teflon  
 (C) SBR is called natural rubber  
 (D) LDPE is called low density polyethylene

**Sol.**

- Q.78** Which is not a rubber polymer-  
 (A) Neoprene (B) Gutta percha  
 (C) Buna-S (D) P.M.M.A.

**Sol.**

- Q.79** Match List – I [polymers] with List – II [monomers] and choose the correct answer from the codes given below the list-  
 List-I [Polymer] List-II [Monomer]

- |                          |                         |
|--------------------------|-------------------------|
| <b>A.</b> P.A.N.         | <b>a.</b> Chloroethene  |
| <b>B.</b> Natural rubber | <b>b.</b> Caprolactum   |
| <b>C.</b> Nylon-6        | <b>c.</b> Isoprene      |
| <b>D.</b> P.V.C.         | <b>d.</b> Acrylonitrile |

Code is-

- |     | A | B | C | D |
|-----|---|---|---|---|
| (A) | d | c | b | a |
| (B) | a | b | c | d |
| (C) | c | d | a | b |
| (D) | b | a | c | d |

**Sol.**

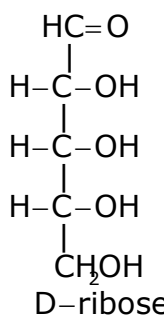
- Q.80** Which of the following is an addition polymer-  
 (A) SBR (B) Glyptals  
 (C) Terylene (D) Nylons

**Sol.**

## Exercise - II

## JEE ADVANCED (Objective)

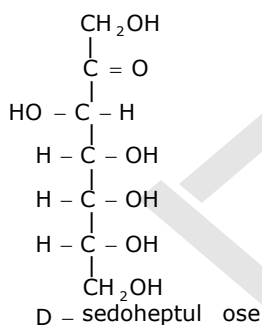
1. Given structure is ?



- (A) Aldopentose (B) Aldohexose  
(C) Ketopentose (D) Aldotetrose

**Sol.**

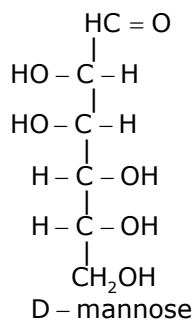
2. Given structure ?



- (A) Aldopentose (B) Ketohexose  
(C) Ketoheptose (D) Ketohexose

**Sol.**

3. Given structure is ?



- (A) Aldopentose (B) Ketohexose  
(C) Ketoheptose (D) Aldohexose

**Sol.**

4. Which of the following is D-glyceraldehyde ?

- (A)  $\begin{array}{c} \text{HC}=\text{O} \\ | \\ \text{HOCH}_2-\text{C}-\text{OH} \\ | \\ \text{H} \end{array}$  (B)  $\begin{array}{c} \text{H} \\ | \\ \text{HO}-\text{C}-\text{CH}_2\text{OH} \\ | \\ \text{HC}=\text{O} \end{array}$   
(C)  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{HC}=\text{O} \end{array}$  (D) A and B both

**Sol.**

5. D-Glucose and L-Glucose are:

- (A) enantiomers  
(B) Distereomers  
(C) D-Glucose is optically active and L-Glucose is optically inactive.  
(D) Not isomers

**Sol.**

6. D-Glucose will form same osazone with -

- (A) D-Mannose (B) D-Fructose  
(C) D-Allose (D) Both (A) and (B)

**Sol.**

7. Relation between D-Glucose &amp; D-Fructose is -

- (A) C<sub>2</sub>-epimer (B) C<sub>3</sub>-epimer  
(C) Functional isomer (D) Positional isomers

**Sol.**

8. Which of following is Oligosaccharides ?

- (A) Glucose (B) Fructose  
(C) Sucrose (D) Starch

**Sol.**

9. Which of the following is D-Glyceraldehyde ?

- (A)  $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{CH} \end{array}$  (B)  $\begin{array}{c} \text{CHO} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{CH}_2 - \text{OH} \end{array}$   
(C)  $\begin{array}{c} \text{CHO} \\ | \\ \text{H} - \text{C} - \text{OH} \\ | \\ \text{CH}_3 \end{array}$  (D)  $\begin{array}{c} \text{CHO} \\ | \\ \text{HO} - \text{C} - \text{H} \\ | \\ \text{CH}_3 \end{array}$

**Sol.**

10. C<sub>2</sub>-epimer of D-Glucose is -

- (A) D-Glucose (B) D-Allose  
(C) D-Altrose (D) D-Mannose

**Sol.**

11. C<sub>3</sub>-epimer of D-Glucose is -

- (A) D-Glucose (B) D-Allose  
(C) D-Altrose (D) D-Mannose

**Sol.**

12. Which of following Carbohydrate is Aldohexose ?

- (A) D-Mannose (B) D-Glucose  
(C) D-Fructose (D) Both (A) and (B)

**Sol.**

13. D-Glucose  $\xrightarrow[\text{H}_2\text{O}]{\text{Br}_2}$  Product is known as -

- (A) D-Glucitol (B) D-Gluconic acid  
(C) D-Glucaric acid (D) Tartaric acid

**Sol.**

14. D-Glucose  $\xrightleftharpoons[\text{D-Glucose}]{\text{HO}^\ominus}$  D-Fructose  $\xrightleftharpoons[\text{D-Glucose}]{\text{HO}^\ominus} (\text{X})$

- (A) D-Allose (B) D-Altrose  
(C) D-Mannose (D) D-Glucose

**Sol.**

15. D-Glucose  $\xrightarrow{5\text{HIO}_4}$  Product is -

- (A) 4HCO<sub>2</sub>H, HCHO (B) 5HCO<sub>2</sub>H, HCHO  
(C) 4HCO<sub>2</sub>H, HCHO (D) 5HCHO, HCO<sub>2</sub>H

**Sol.**

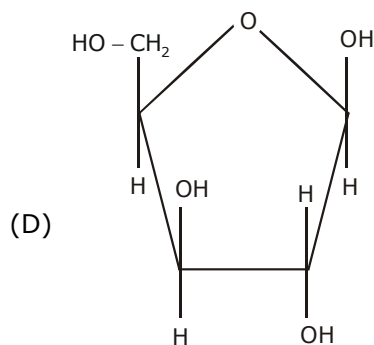
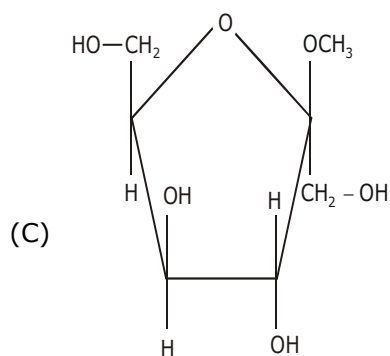
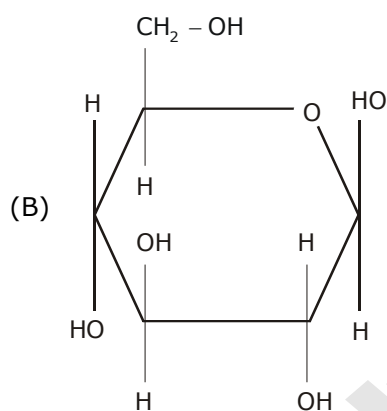
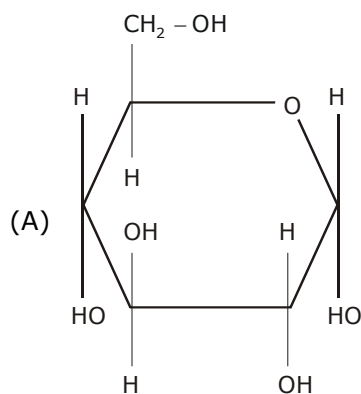
16. Which of following pair give same Osazone-

- (A) D-Glucose, Fructose (B) D-Glucose, D-Mannose  
(C) D-Allose, D-Altrose (D) All

**Sol.**



## Comprehension (Q.17 to Q.20)



Sol.

17. Relation between (A) and (B) is -

- (A) Anomers (B) Positional isomer  
(C) Functional isomer (D) Enantiomer

Sol.

18. Structure of B-D-Glucose pyranose is -

- (A) A (B) B  
(C) C (D) D

Sol.

19. Which of compound not undergo mutarotation -

- (A) A (B) B  
(C) C (D) D

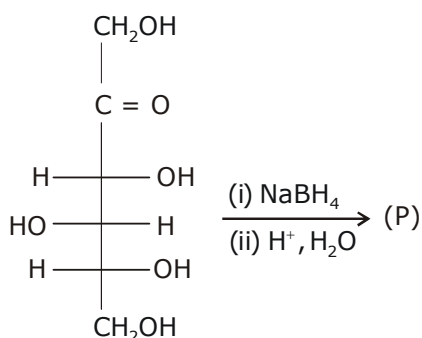
Sol.

20. How many mole of acetic anhydride will consumed when it reacts with compound (A)

- (A) 3 (B) 4  
(C) 5 (D) 6

Sol.

21.



D-sorbose

Number of stereoisomer of product (P) is -

- (A) 4 (B) 10  
(C) 12 (D) 16

**Sol.**

22. The main structural features of proteins is -

- (A) Ester linkage (B) Ether linkage  
(C) Peptide linkage (D) All of these

**Sol.**

23. Which compound can exist in a dipolar (Zwitterion) structure ?

- (A)  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{N}=\text{CH}_2)\text{COOH}$   
(B)  $(\text{CH}_3)_2\text{CHCH}(\text{NH}_2)\text{COOH}$   
(C)  $\text{C}_6\text{H}_5\text{CONHCH}_2\text{COOH}$   
(D)  $\text{HOOCCH}_2\text{CH}_2\text{COCOCH}_2\text{COOH}$

**Sol.**

24. Vitamins C is chemically -

- (A) Ascorbic acid (B) Citric acid  
(C) Aspirin (D) Aspartic acid

**Sol.**

25.

In an amino acid, the carboxylic group ionises at  $p^{ka_1} = 2.34$  and ammonium ion at  $p^{ka_2} = 9.60$ . The iso electric point of the amino acid is at pH -

- (A) 5.97 (B) 2.34  
(C) 9.60 (D) 6.97

**Sol.**

26.

Which statement is incorrect about peptide bond ?

- (A) C-N bond length in proteins is longer than usual bond length of C-N bond  
(B) Spectroscopic analysis shows planer structure of  $-\text{C}-\text{NH}-$  bond



- (C) C-N bond length in proteins is smaller than usual bond length of C-N bond  
(D) None of these

**Sol.**

27.

A triglyceride can have how many different acyl groups ?

- (A) 3 (B) 2  
(C) 1 (D) 4

**Sol.**

28.

Which one of the following is natural polymer-

- (A) Starch (B) Nylon-6  
(C) Kodel (D) Buna-S, SBR

**Sol.**

29. Which of the following is homopolymer ?  
(A) Starch (B) Polystyrene  
(C) Orlon (D) All of these

Sol.

30. Which of the following monomers can undergoes radical, cationic as well as anionic polymerisation with equal ease ?

- (A)  $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} = \text{CH}_2$  (B)  $\text{C}_6\text{H}_5 - \text{CH} = \text{CH}_2$   
(C)  $\text{CH}_2 = \text{CH} - \text{CN}$  (D)  $\text{CH}_2 = \text{CH}_2$

Sol.

31. Ziegler-Natta catalyst is -

- (A)  $\text{R}_3\text{Al}$  (B)  $\text{TiCl}_4$   
(C)  $\text{R}_3\text{Al} + \text{TiCl}_4$  (D)  $\text{R}_3\text{B} + \text{TiCl}_2$

Sol.

32. Monomer of Teflon is -

- (A) Monochloroethene  
(B) 1,2-Difluoroethene  
(C) 1, 1, 2-Trifluoroethene  
(D) Tetrafluoroethene

Sol.

33. Orlon is polymer of -

- (A) Styrene (B)  $\text{CF}_2 = \text{CF}_2$   
(C) Vinyl chloride (D) Acrylonitrile

Sol.

34. Intermolecular force present in nylon-66 is-  
(A) vander Waal (B) Hydrogen bond  
(C) Dipole-Dipole interactions  
(D) Sulphide linkage

Sol.

35. Nylon-66 is made by using -

- (A) Phenol (B) Benzaldehyde  
(C) Adipic acid (D) Succinic acid

Sol.

36. Polymer which has amide linkage is -

- (A) Nylon-66 (B) Terylene  
(C) Teflon (D) Bakelite

Sol.

37. Bekelite is prepared by the reaction between-

- (A) Phenol and formaldehyde  
(B) Ethylene glycol and dimethylphthalate  
(C) Urea and formaldehyde  
(D) Tetramethylene glycol and hexamethylene diamine

Sol.

38. Natural rubber is a polymer of -  
(A) Butadiene (B) Ethyne  
(C) Styrene (D) Isoprene

Sol.

Sol.

39. Terylene is a condensation polymer of ethylene glycol and  
(A) Benzoic acid (B) Phthalic acid  
(C) Salicylic acid (D) Terephthalic acid

Sol.

43. Which one of the following is a polyamide?  
(A) Teflon (B) Nylon-66  
(C) Terylene (D) Bakelite

Sol.

44. Glycosidic linkage is present in -  
(A) Sucrose (B) Maltose  
(C) Lactose (D) All

Sol.

40. Cellulose acetate is a -  
(A) Natural polymer  
(B) Semisynthetic polymer  
(C) Synthetic polymer  
(D) Plasticiser

Sol.

45. Which of the following amino acid has lowest isoelectric point ?  
(A) Lysine (B) Aspartic acid  
(C) glycine (D) Alanine

Sol.

41. A condensation polymer among the following polymers is -  
(A) Teflon (B) Polystyrene  
(C) PVC (D) Dacron

Sol.

46. Protein on hydrolysis give -  
(A)  $\alpha$ -amino acid (B)  $\beta$ -amino acid  
(C)  $\gamma$ -amino acid (D) All

Sol.

42. In elastomer, intermolecular forces are -  
(A) Nil (B) Weak  
(C) Strong (D) Very strong

47. Which of the following amino acid is optically inactive -  
(A) Glycine (B) Alanine  
(C) Valine (D) Leucine

**Sol.**

48. Peptide linkage is present in -  
(A) Protein (B) Nylon-6, 6  
(C) Sucrose (D) both (A) & (B)

**Sol.**

49. Product obtained by hydrolysis of lactose are -  
(A) Glucose & fructose (B) Glucose, mannose  
(C) Mannose & fructose (D) Galactose, Glucose

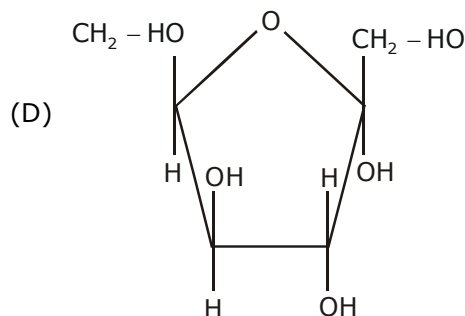
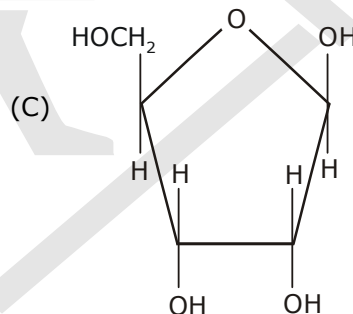
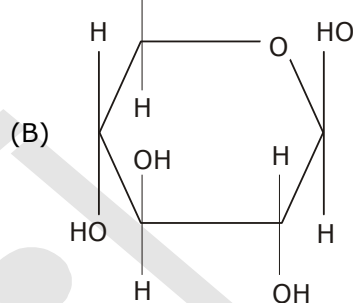
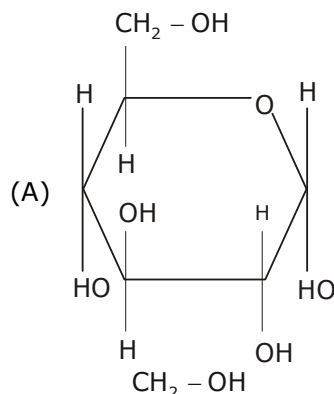
**Sol.**

50. Which of the following is an amino acid?

- (A)  $\text{NH}_2\text{-CH}_2\text{-CO}_2\text{H}$   
(B)  $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-CO}_2\text{H}$   
(C)  $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CO}_2\text{H}$  (D) All

**Sol.**

51. Which of the following is the structure of  $\beta$ -D-Glucopyranose?

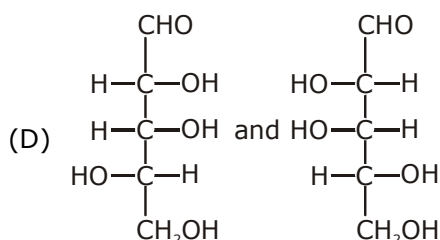
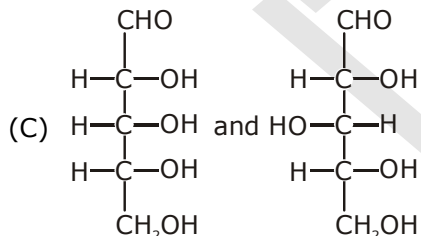
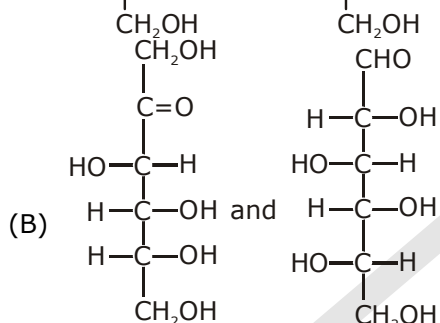
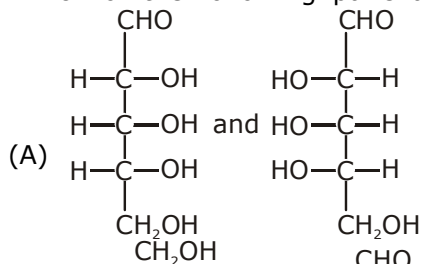




61. Glucose and mannose are  
 (A) Anomers (B) Positional isomers  
 (C) Functional isomers (D) Epimers

Sol.

62. Which of the following pairs are epimers



Sol.

63. Glucose molecule reacts with X number of molecule of phenylhydrazine to yield osazone. The value of X is  
 (A) Three (B) Two  
 (C) One (D) Four

Sol.

64. Which of the following reagents cannot distinguish between glucose and fructose ?  
 (A) Tollens reagent (B) Fehling solution  
 (C) Benedict solution (D) All of these

Sol.

65. Cellulose is a polymer of  
 (A) Glucose (B) Fructose  
 (C) Ribose (D) Sucrose

Sol.

66. Which of the following is an example of Ketohexose ?  
 (A) Mannose (B) Galactose  
 (C) Maltose (D) Fructose

Sol.

67. When glucose reacts with bromine water, the main product is  
 (A) Acetic acid (B) Saccharic acid  
 (C) Glyceraldehyde (D) Gluconic acid

Sol.

68. All monosaccharide ..... Tollens reagent

- (A) oxidises (B) reduces  
(C) condense with (D) add to

Sol.

69. The number of chiral centres in (+) glucose is

- (A) 4 (B) 3  
(C) 2 (D) 1

Sol.

70. Protein is polymer of

- (A) Amino acid (B)  $\alpha$ -Amino acid  
(C)  $\gamma$ -Amino acid (D)  $\beta$ -Amino acid

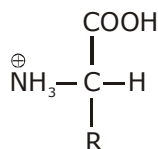
Sol.

71. Amino acid may be

- (A) Neutral (B) Basic  
(C) Acid (D) Any one of these

Sol.

72. The given structure of  $\alpha$ -amino acid will exist at which pH ?



- (A) 7 (B) 14  
(C) 2-3 (D) 12

Sol.

73. Peptide linkage is

- (A)  $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{O}- \end{array}$  (B)  $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{NH}_2 \end{array}$   
(C)  $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{NH}-\text{NH}_2 \end{array}$  (D)  $\begin{array}{c} \text{O} \\ || \\ -\text{C}-\text{NH}- \end{array}$

Sol.

74. Complete hydrolysis of cellulose gives

- (A) L-glucose (B) D-fructose  
(C) D-ribose (D) D-glucose

Sol.

75. Number of chiral carbons in  $\beta$ -D-(+)-glucose is

- (A) six (B) three  
(C) four (D) five

Sol.

76. The pair of compounds in which both the compounds give positive test with Tollen's reagent is

- (A) glucose and sucrose  
(B) fructose and sucrose  
(C) acetophenone and hexanal  
(D) glucose and fructose

Sol.

77. Among cellulose, polyvinyl chloride, nylon, and natural rubber, the polymer in which the intermolecular force of attraction is the weakest is

- (A) polyvinyl chloride (B) natural rubber  
(C) nylone (D) cellulose



Sol.

78. D-Glucose & L-Glucose are  
 (A) Enantiomers (B) Diastereomers  
 (C) Epimers (D) Anomers

Sol.

79. Identify the pair of Epimers  
 (A) D-Glucose & D-Fructose  
 (B) D-Glucose & L-Glucose  
 (C) D-Glucose & D-Mannose  
 (D) D-Glucose & D-Glucose

Sol.

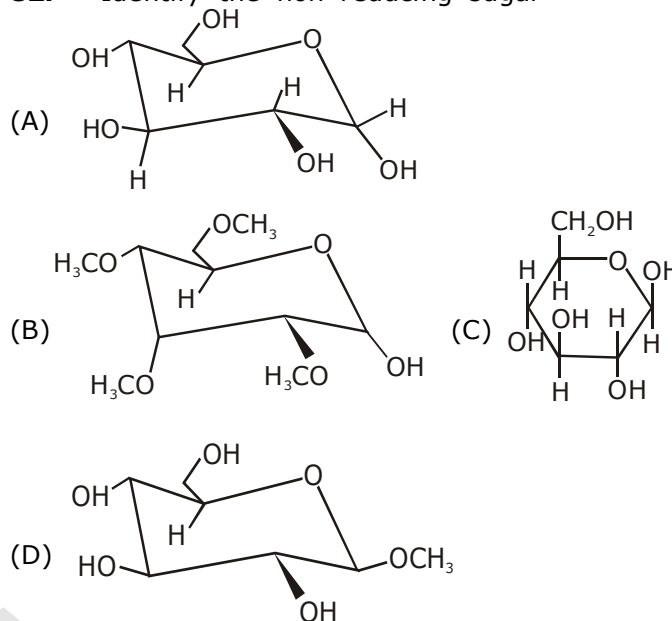
80. The number of Stereogenic centres in  $\alpha$ -D-Glucose are  
 (A) 4 (B) 5  
 (C) 3 (D) 2

Sol.

81.  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose are  
 (A) Epimers (B) Anomers  
 (C) Enantiomers (D) Acetals

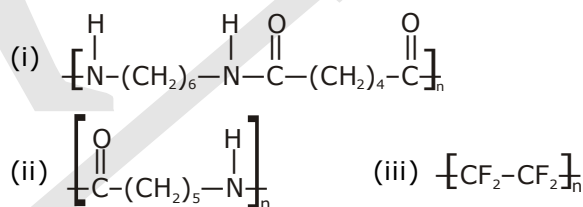
Sol.

82. Identify the non reducing sugar



Sol.

83. Write the names of monomers of the following polymers :



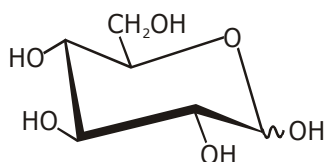
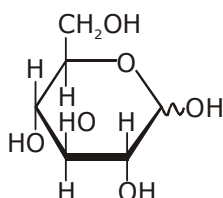
Sol.

84. Classify the following as addition and condensation polymers: Terylene, Bakelite, Polyvinyl chloride, Polythene.

Sol.

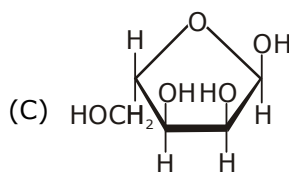
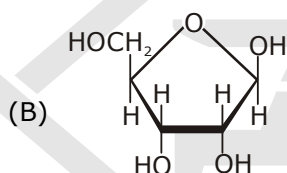
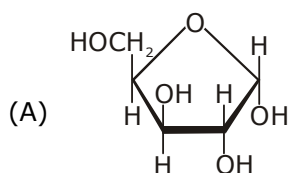
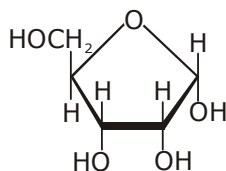
**EXERCISE – III****SUBJECTIVE PROBLEMS (JEE ADVANCED)****Comprehension (Q.1 to Q.3)**

It is convenient at times to represent the cyclic structures of a monosaccharide without specifying whether the configuration of the anomeric carbon atom is  $\alpha$  or  $\beta$ . When we do this, we shall use formulas such as the following



~ Indicates  $\alpha$  or  $\beta$  (three-dimensional view not specified)

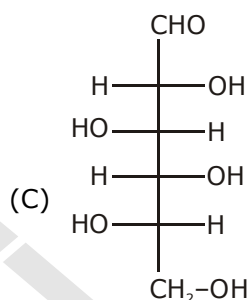
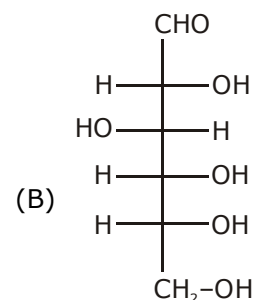
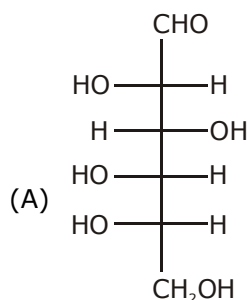
1. Which of the following represents the anomer of the compound shown ?



(D) None of these

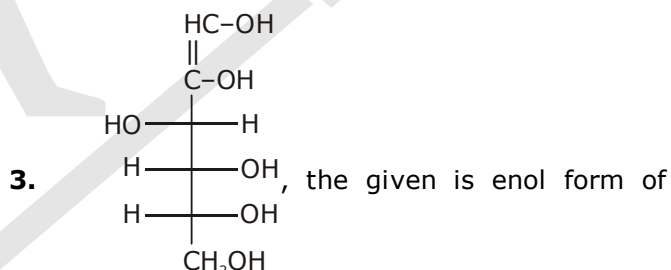
**Sol.**

2. What is the structure of L-Glucose ?



(D) None of these

**Sol.**



- (A) D-glucose  
(C) D-fructose

- (B) D-mannose  
(D) All of these

**Sol.**

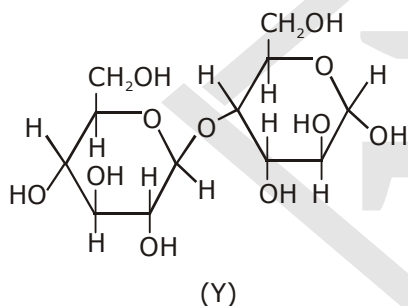
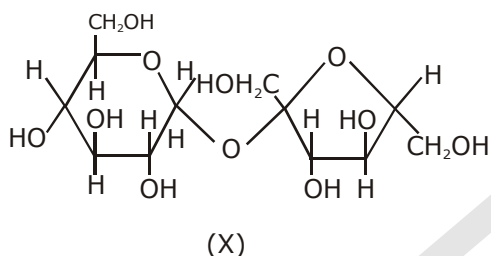
**MCQ :**

4. Which of the following pair forms the same osazone with phenylhydrazine

- (A) D-Glucose and D-Fructose  
 (B) D-Fructose and D-Mannose  
 (C) D-Glucose and D-Mannose  
 (D) D-Glucose and D-Galactose

**Sol.**

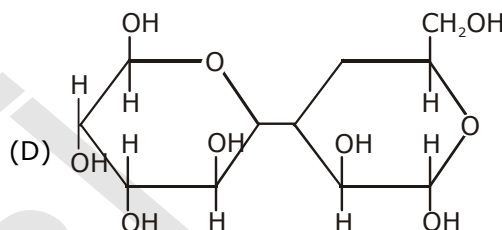
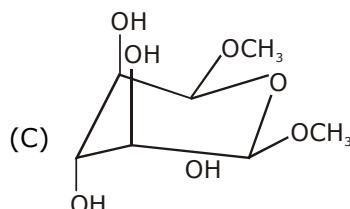
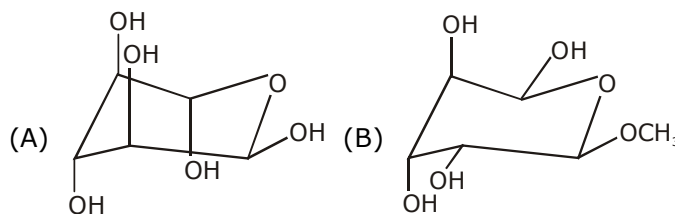
5. The correct statement(s) about the following sugars X and Y is (are)



- (A) X is a reducing sugar and Y is a non-reducing sugar  
 (B) X is a non-reducing sugar and Y is a reducing sugar  
 (C) The glucosidic linkages in X and Y are  $\alpha$  and  $\beta$ , respectively  
 (D) The glucosidic linkages in X and Y are  $\beta$  and  $\alpha$ , respectively

**Sol.**

6. Which of the following compound give positive Tollen's test ?



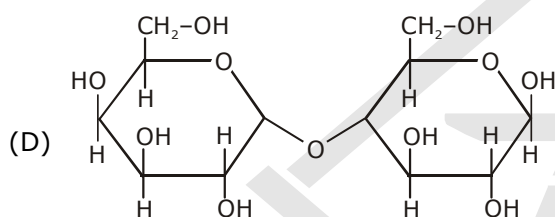
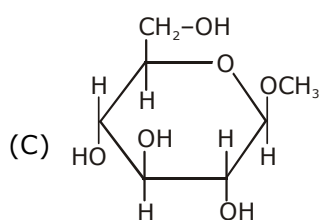
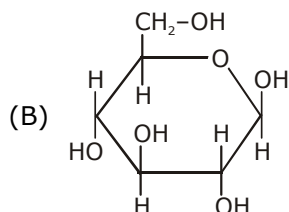
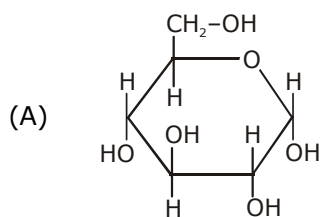
**Sol.**

**Match the column :****7. Column-I****Column-II**

- (A) Nylon -6, 6 (P) Condensation polymerization  
 (B) styrene (Q) Addition polymerization  
 (C) Bakelite (R) Homo polymer  
 (D) Teflon (S) Co-polymer

**Sol.**

## 8. Column-I



## Column-II

- (P) It will undergo osazone formation  
 (Q) When undergo acetylation reaction with acetic anhydride molecular weight increases by 210  
 (R) It is reducing sugar  
 (S) It is known as  $\alpha$ -D-Glucopyranose  
 (T) It is not reducing sugar & not show the mutarotation

Sol.

## 9. Column-I

(A) Sucrose  $\xrightarrow{\text{H}_3\text{O}^+}$ (B) Maltose  $\xrightarrow{\text{H}_3\text{O}^+}$ (C) Lactose  $\xrightarrow{\text{H}_3\text{O}^+}$ 

## Column-II

- (P) Product is glucose + Fructose  
 (Q) Product is 2 Glucose  
 (R) Product is Glucose + Galactose  
 (S) Oligo saccharides

Sol.

## 10. Column-I

- (A) Terylene  
 (B) Stryrene  
 (C) Bakellite  
 (D) Teflon

Sol.

## Column-II

- (P) Condensation polymerization  
 (Q) Addition polymerization  
 (R) Homo polymer  
 (S) Co-polymer

**EXERCISE – IV****PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

**Q.1** The functional group, which is found in amino acid is - **[AIEEE-2002]**

- (A)  $\text{-COOH}$  group      (B)  $\text{-NH}_2$  group  
(C)  $\text{-CH}_3$  group      (D) Both (A) and (B)

**Sol.**

**Q.2** RNA contains - **[AIEEE-2002]**

- (A) Uracil, Ribose  
(B) Thiamine, Ribose  
(C) Cytocine, Deoxyribose  
(D) Adenine, Deoxyribose

**Sol.**

**Q.3** Complete hydrolysis of cellulose gives - **[AIEEE-2003]**

- (A) D-glucose      (B) L-glucose  
(C) D-fructose      (D) D-ribose

**Sol.**

**Q.4** The reason for double helical structure of DNA is operation of - **[AIEEE-2003]**

- (A) Hydrogen bonding  
(B) Electrostatic attractions  
(C) vander Waal's forces  
(D) Dipole-dipole interaction

**Sol.**

**Q.5** Coordination compounds have great importance in biological systems, In this context which of the following statements is incorrect ? **[AIEEE-2004]**

- (A) Chlorophylls are green pigments in plants and contain calcium  
(B) haemoglobin is the red pigment of blood and contains iron  
(C) Cyanocobalamin is  $\text{B}_{12}$  and contains cobalt  
(D) Carboxypeptidase-A is an enzyme and contains zinc

**Sol.**

**Q.6** Which base is present in RNA but not in DNA ? **[AIEEE-2004]**

- (A) Uracil      (B) Cytosine  
(C) Guanine      (D) Thymine

**Sol.**

**Q.7** Insulin production and its action in human body are responsible for the level of diabetes. This compound belongs to which of the following categories ? **[AIEEE-2004]**

- (A) A co-enzyme (B) A hormone  
(C) An enzyme (D) An antibiotic

**Sol.**

**Q.8** Identify the correct statement regarding enzymes : **[AIEEE-2004]**

- (A) Enzymes are specific biological catalysts that can normally function at very high temperatures ( $T \sim 1000\text{ K}$ )  
(B) Enzymes are normally heterogeneous catalysts that are very specific in their action  
(C) Enzymes are specific biological catalysts that cannot be poisoned  
(D) Enzymes are specific biological catalysts that possess well-defined active sites

**Sol.**

**Q.9** In both DNA and RNA, heterocyclic base and phosphate ester linkages are at – **[AIEEE-2005]**

- (A)  $C_2'$  and  $C_5'$  respectively of the sugar molecule  
(B)  $C_5'$  and  $C_2'$  respectively of the sugar molecule  
(C)  $C_5'$  and  $C_1'$  respectively of the sugar molecule  
(D)  $C_3'$  and  $C_5'$  respectively of the sugar molecule

**Sol.**

**Q.10** The pyrimidine bases present in DNA are – **[AIEEE 2006]**

- (A) cytosine and guanine  
(B) cytosine and thymine  
(C) cytosine and uracil  
(D) cytosine and adenine

**Sol.**

**Q.11** The term anomers of glucose refers to – **[AIEEE 2006]**

- (A) a mixture of (D)-glucose and (L)-glucose  
(B) enantiomers of glucose  
(C) isomers of glucose that differ in configuration at carbon one (C-1)  
(D) isomers of glucose that differ in configurations at carbons one and four (C-1 and C-4)

**Sol.**

**Q.12** The secondary structure of a protein refers to – **[AIEEE 2007]**

- (A)  $\alpha$ -helical backbone  
(B) hydrophobic interactions  
(C) sequence of  $\alpha$ -amino acids  
(D) fixed configuration of the polypeptide backbone

**Sol.**

**Q.13**  $\alpha$ -D-(+)-glucose and  $\beta$ -D-(+)-glucose are  
[AIEEE 2008]

- (A) epimers (B) anomers  
(C) enantiomers (D) conformers

**Sol.**

**Q.14** The two functional groups present in a typical carbohydrate are :  
[AIEEE 2009]

- (A) -OH and -COOH (B) -CHO and -COOH  
(C) >C=O and -OH (D) -OH and -CHO

**Sol.**

**Q.15** Which amino acid is chiral ? [AIEEE-2009]

- (A) Alanine (B) Valine  
(C) Proline (D) Histidine

**Sol.**

**Q.16** Biuret test is *not* given by - [AIEEE 2010]

- (A) proteins (B) carbohydrates  
(C) polypeptides (D) urea

**Sol.**

**Q.17** The presence or absence of hydroxy group on which carbon atom of sugar differentiates RNA and DNA ? [AIEEE 2011]

- (A) 1<sup>st</sup> (B) 2<sup>nd</sup> (C) 3<sup>er</sup> (D) 4<sup>th</sup>

**Sol.**

**Q.18** Which one of the following statements is correct ? [AIEEE-2012]

- (A) All amino acids are optically active  
(B) All amino acids except glycine are optically active  
(C) All amino acids except glutamic acid are optically active  
(D) All amino acids except lysine are optically active

**Sol.**

**Q.19** Which of the following compounds can be detected by Molisch's test ? [AIEEE-2012]

- (A) Sugars (B) Amines  
(C) Primary alcohols (D) Nitro compounds

**Sol.**

**Q.20** Monomers are converted to polymer by - [AIEEE-2003]

- (A) Hydrolysis of monomers  
(B) Condensation reaction between monomers  
(C) Protonation of monomers  
(D) None is correct

Sol.

**Q.21** Nylon threads are made of – [AIEEE-2003]

- (A) Polyamide polymer (B) Polyethylene polymer  
(C) Polyvinyl polymer (D) Polyester polymer

Sol.

**Q.22** Which of the following is a polyamide ?

[AIEEE-2005]

- (A) Nylon-66 (B) Teflon  
(C) Bakelite (D) Terylene

Sol.

**Q.23** Which of the following is fully fluorinated polymer- [AIEEE-2005]

- (A) Teflon (B) Neoprene  
(C) PVC (D) Thiokol

Sol.

**Q.24** Bakelite is obtained from phenol by reacting with [AIEEE 2008]

- (A)  $\text{CH}_3\text{CHO}$  (B)  $\text{CH}_3\text{COCH}_3$   
(C)  $\text{HCHO}$  (D)  $(\text{CH}_2\text{OH})_2$

Sol.

**Q. 25** Buna-N synthetic rubber is a copolymer of -

[AIEEE 2009]

- (A)  $\text{H}_2\text{C}=\overset{\text{Cl}}{\underset{|}{\text{CH}}}-\text{C}=\text{CH}_2$  and  $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$   
(B)  $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$  and  $\text{H}_5\text{C}_6-\text{CH}=\text{CH}_2$   
(C)  $\text{H}_2\text{C}=\text{CH}-\text{CN}$  and  $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$   
(D)  $\text{H}_2\text{C}=\text{CH}-\text{CN}$  and  $\text{H}_2\text{C}=\text{CH}-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}_2$

Sol.

**Q.26** The species which can best serve as an initiator for the cationic polymerization is

[AIEEE-2012]

- (A)  $\text{HNO}_3$  (B)  $\text{AlCl}_3$   
(C)  $\text{BuLi}$  (D) None of these

Sol.

**Q.27** Synthesis of each molecule of glucose in photosynthesis involves: [AIEEE-2013]

- (A) 5 molecules of ATP  
(B) 18 molecules of ATP  
(C) 10 molecules of ATP  
(D) 8 molecules of ATP

Sol.



## LEVEL – II

## JEE ADVANCED

1. Which of the following pairs given positive Tollen's test ? [IIT 2004]

- (A) Glucose, sucrose (B) Glucose, fructose  
(C) Hexanal, acetophenone  
(D) Fructose, sucrose

Sol.

2. The two forms of D-glucopyranose obtained from the solution of D-glucose are called : [IIT 2005]

- (A) isomer (B) anomer  
(C) epimer (D) enantiomer

Sol.

3. Column-I

- (A) Cellulose  
(B) nylon-6, 6  
(C) protein  
(D) sucrose

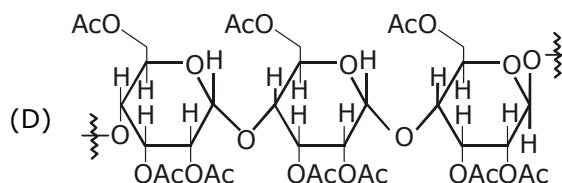
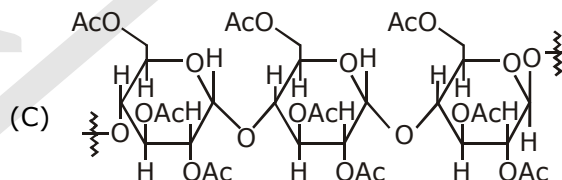
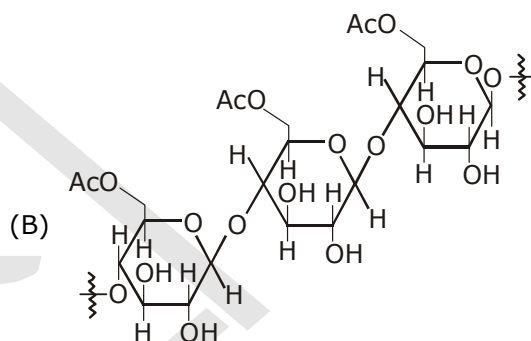
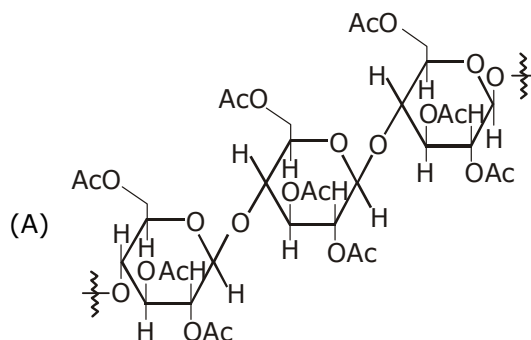
Sol.

Column-II

- (P) natural polymer  
(Q) synthetic polymer  
(R) amide linkage  
(S) glycoside linkage

[IIT 2006]

4. Cellulose upon acetylation with excess acetic anhydride/ $H_2SO_4$  (catalytic) gives cellulose triacetate whose structure is [IIT 2007]



Sol.

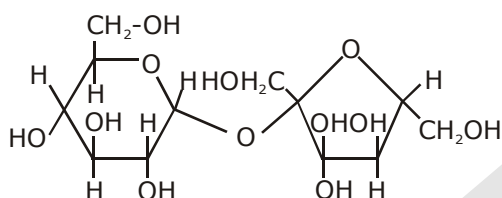
5. Among cellulose, poly (vinyl chloride), nylon and natural rubber, the polymer in which the intermolecular force of attraction is weakest is :

[IIT 2008]

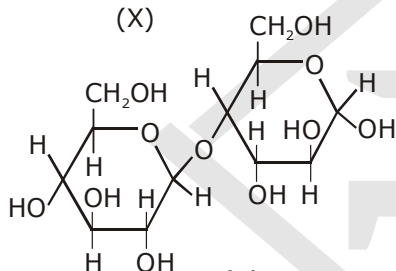
- (A) nylon (B) Poly (vinyl chloride)  
(C) cellulose (D) natural rubber

Sol.

6. The correct statement(s) about the following sugars X and Y is (are) [IIT 2009]



(X)



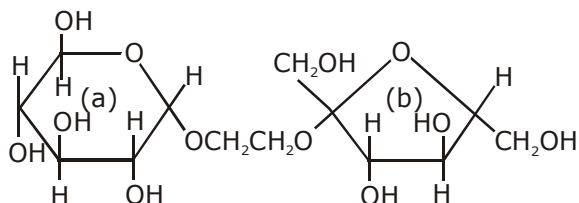
(Y)

- (A) X is a reducing sugar and Y is a non-reducing sugar  
(B) X is a non-reducing sugar and Y is a reducing sugar  
(C) The glucosidic linkages in X and Y are  $\alpha$  and  $\beta$ , respectively  
(D) The glucosidic linkages in X and Y are  $\beta$  and  $\alpha$ , respectively

Sol.

7. The correct statement about the following disaccharide is

[IIT 2010]

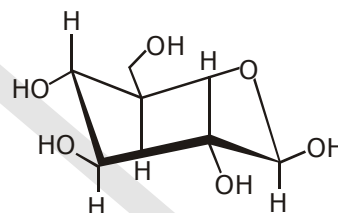


- (A) Ring (a) is pyranose with  $\alpha$ -glycosidic link  
(B) Ring (a) is furanose with  $\alpha$ -glycosidic link  
(C) Ring (b) is furanose with  $\alpha$ -glycosidic link  
(D) Ring (b) is pyranose with  $\beta$ -glycosidic link

Sol.

8. The following carbohydrate is

[IIT 2011]



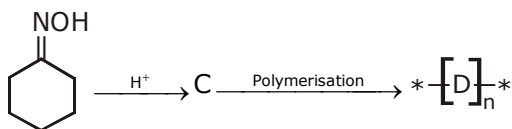
- (A) a ketohexose (B) an aldohexose  
(C) an  $\alpha$ -furanose (D) an  $\alpha$ -pyranose

Sol.

9. Give the structures of the products in the following reaction  
Sucrose  $\xrightarrow{H^+}$  A+B [IIT 2000]

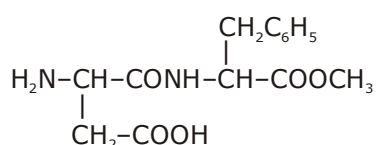
Sol.

10. Give the structure of the products in the following reaction [IIT 2000]



Sol.

11. Aspartame, an artificial sweetener, is a peptide and has the following structure :



[IIT 2001]

- Identify the four functional groups.
- Write the zwitter ionic structure.
- Write the structure of the amino acids obtained from the hydrolysis of aspartame.
- Which of the two amino acids is more hydrophobic?

Sol.

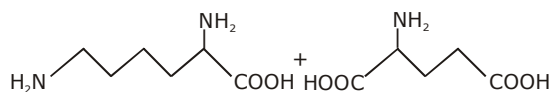
12. Write the structure of alanine at pH = 2 and pH = 10. [IIT 2002]

Sol.

13. Write down the heterogeneous catalyst involved in the polymerization of ethylene. [IIT 2003]

Sol.

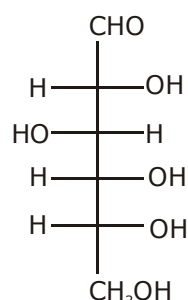
14. Following two amino acids lysine and glutamine form dipeptide linkage. What are two possible dipeptides ?



[IIT 2003]

Sol.

15. The structure of D-glucose is as follows : [IIT 2004]

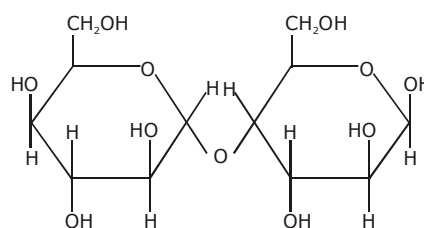


- Draw the structure of L-glucose
- Give the reaction of L-glucose with Tollen's reagent

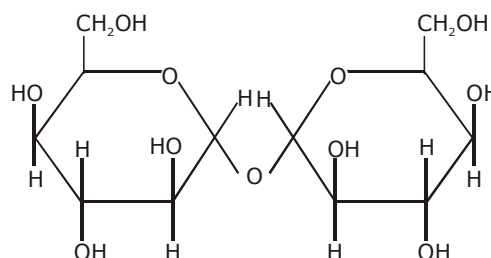
Sol.

16. Which of the following disaccharide will not reduce Tollen's reagent ?

(A)



(B)



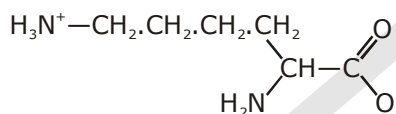
Sol.

17. Monomer A of a polymer on ozonolysis yields two moles of HCHO and one mole of CH<sub>3</sub>COCHO.

- (a) Deduce the structure of A.  
(b) Write the structure of "all cis"-form of polymer of compound A. [IIT 2005]

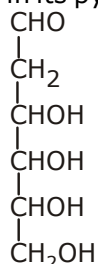
Sol.

18. What is the total number of basic groups in the following form of lysine? [IIT 2010]



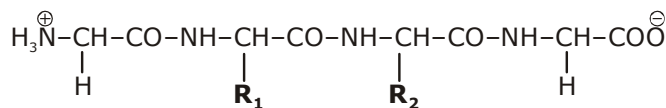
Sol.

19. When the following aldohexose exists in its D-configuration, the total number stereoisomers in its pyranose form is [IIT 2012]



Sol.

20. The substituents **R<sub>1</sub>** and **R<sub>2</sub>** for nine peptides are listed in the table given below. How many of these peptides are positively charged at pH = 7.0? [IIT 2012]



Peptide	R <sub>1</sub>	R <sub>2</sub>
I	H	H
II	H	CH <sub>3</sub>
III	CH <sub>2</sub> COOH	H
IV	CH <sub>2</sub> CONH <sub>2</sub>	(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub>
V	CH <sub>2</sub> CONH <sub>2</sub>	CH <sub>2</sub> CONH <sub>2</sub>
VI	(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub>	(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub>
VII	CH <sub>2</sub> COOH	CH <sub>2</sub> CONH <sub>2</sub>
VIII	CH <sub>2</sub> OH	(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub>
IX	(CH <sub>2</sub> ) <sub>4</sub> NH <sub>2</sub>	CH <sub>3</sub>

Sol.

21. The total number of lone-pairs of electrons in melamine is [IIT(Advance) 2013]

Sol.

22. A tetrapeptide has -COOH group on alanine. This produces glycine (Gly), valine (Val), phenyl alanine (Phe) and alanine (Ala), on complete hydrolysis. For this tetrapeptide, the number of possible sequences (primary structures) with -NH<sub>2</sub> group attached to a chiral center is [IIT(Advance) 2013]

Sol.

**ANSWER KEY****EXERCISE - I**

Ques.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	C	A	A	C	A	C	C	D	D	D	C	B	B	D	C	B	D	A	D	B
Ques.	21	22	23	24	25	26	27	28	29	30										
Ans.	C	A	B	D	C	B	D	A	D	D										

Ques.	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
Ans.	C	D	D	C	C	A	D	D	B	B	C	B	A	D	B	A	C	C	D	A
Ques.	51	52	53	54	55	56	57	58	59	60										
Ans.	B	D	B	A	B	A	A	A	B	A										

Qus.	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
Ans.	A	B	C	C	B	A	D	B	A	D	A	B	C	C	A
Qus.	76	77	78	79	80										
Ans.	B	C	D	A	A										

**EXERCISE - II**

1.	A	2.	C	3.	D	4.	C	5.	A	6.	D	7.	C
8.	C	9.	B	10.	D	11.	B	12.	D	13.	B	14.	C
15.	B	16.	D	17.	A	18.	B	19.	C	20.	C	21.	B
22.	C	23.	B	24.	A	25.	A	26.	A	27.	A	28.	A
29.	D	30.	B	31.	C	32.	D	33.	D	34.	B	35.	C
36.	A	37.	A	38.	D	39.	D	40.	B	41.	D	42.	B
43.	B	44.	D	45.	B	46.	D	47.	A	48.	D	49.	D
50.	D	51.	B	52.	B	53.	A	54.	B	55.	C	56.	D
57.	D	58.	C	59.	D	60.	D	61.	D	62.	C	63.	A
64.	D	65.	A	66.	D	67.	D	68.	B	69.	A	70.	B
71.	D	72.	C	73.	D	74.	D	75.	D	76.	D	77.	B
78.	A	79.	C	80.	B	81.	B	82.	D				

83. (i) Hexamethylene diamine and adipic acid, (ii) Caprolactam, (iii) Tetrafluoroethene

84. Addition polymers : Polyvinyl chloride, Polythene  
Condensation polymers : Terylene, Bakelite

**EXERCISE-III**

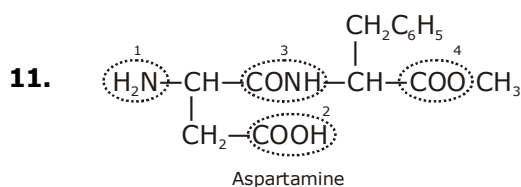
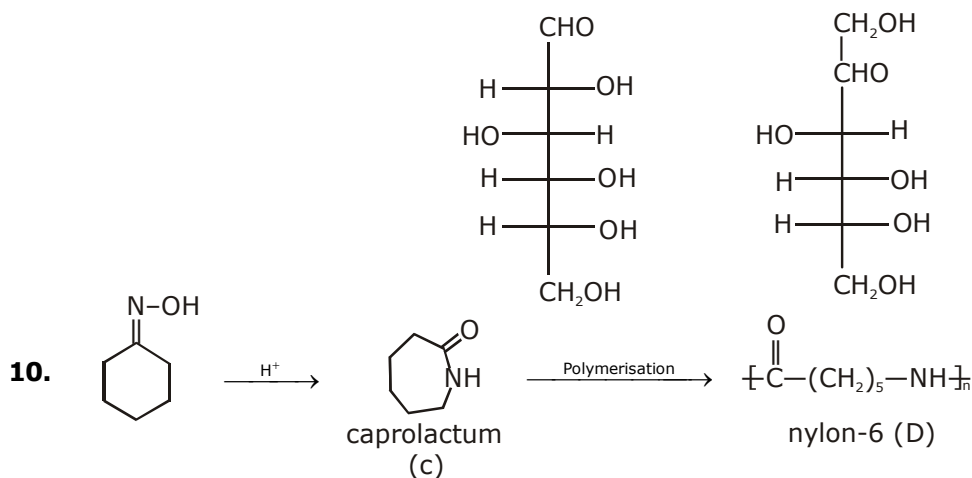
1.	B	2.	A	3.	D	4.	ABC	5.	BC	6.	ABD
7.	A-P, S; B-Q, R; C-P, S; D-Q,R						8.	A-P,Q,R,S; B-P,Q,R; C-T Ans; D-P,R			
9.	A-PS; B-QS; C-RS						10.	A-PS; B-QR; C-PS; D-QR			

**EXERCISE - IV  
Level-I**

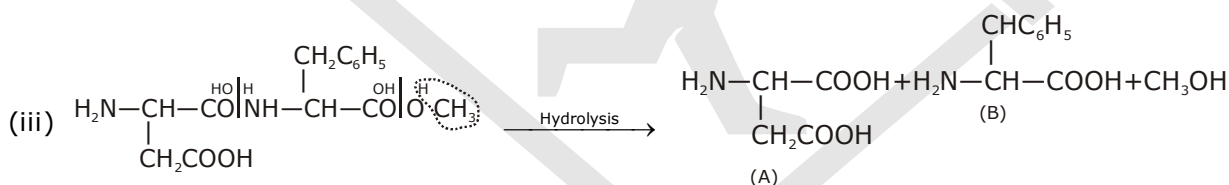
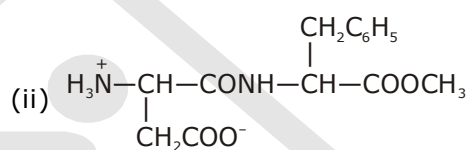
Q.No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	
Ans.	D	A	A	A	A	A	B	D	D	B	C	A	B	C	A,B,C,D	B	B	B	A	
20	21	22	23	24	25	26	27													
B	A	A	A	C	C	B	B													

## Level-II

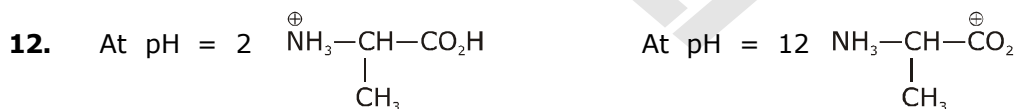
1. B                      2. B                      3. A→P,S; B→Q,R; C→P,R; D→S                      4. A  
 5. D                      6. BC                      7. A                      8. B  
 9. Sucrose  $\xrightarrow[\text{H}_2\text{O}]{\text{H}^+}$  D-glucose + D-fructose



- (i)  $\text{NH}_2$ -gp. (1)-amino gp.  
 $-\text{COOH}$  gp. (2) -carboxyl gp.  
 $-\text{CONH}$  gp. (3) -2°-amide gp.  
 $-\text{COOH}$  gp. (4) -ester gp.

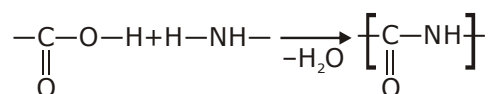


- (iv) B is more hydrophobic due to presence of larger organic gp., benzyl gp. ( $\text{C}_6\text{H}_5\text{CH}_2-$ ).



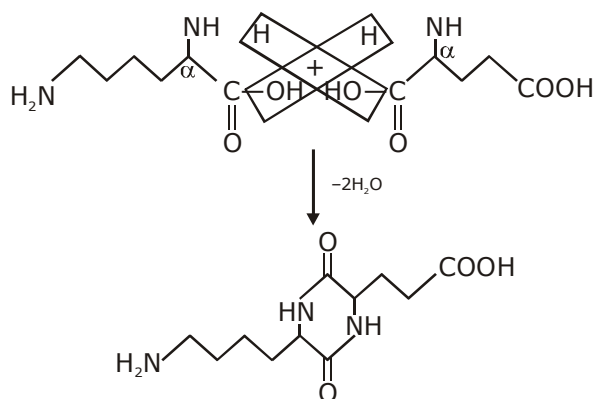
13.  $n\text{CH}_2 = \text{CH}_2 \xrightarrow[\text{Ziegler Natta Catalyst}]{\text{R}_3\text{Al} + \text{TiCl}_4} \text{-(CH}_2\text{-CH}_2\text{)}_n$  Ziegler Natta catalyst ( $\text{R}_3\text{Al} + \text{TiCl}_4$ ) acts as heterogenous catalyst. While Willikinson's Catalyst ( $(\text{Ph}_3\text{P})_3\text{RhCl}$ ) acts as homogenous catalyst.

14. Peptide linkage is  $-\text{NH}-\text{C}(=\text{O})-$  and it is formed by the condensatoin between  $-\text{NH}_2$  group and  $-\text{COOH}$  group as follows :

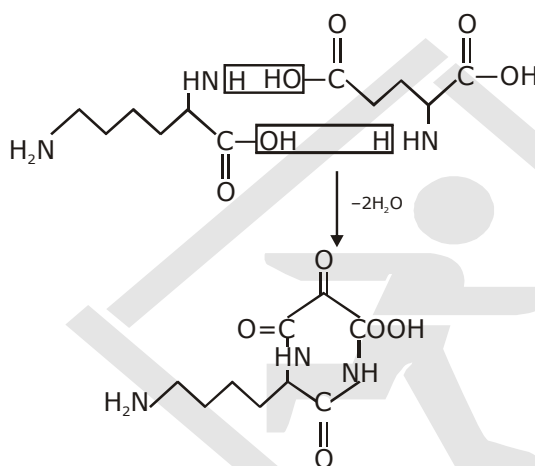


In given amino acids liosine and glutamine the two possible dipeptides are formed as follows:

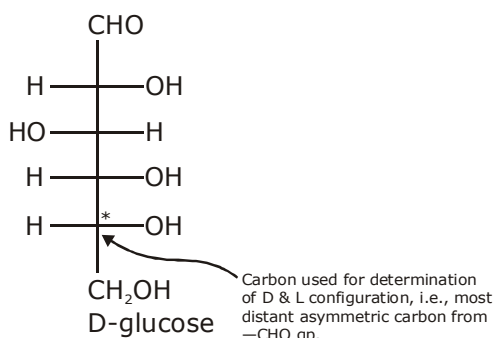
(i) When both  $\text{NH}_2$  gp.  $\alpha$  to  $-\text{COOH}$  are condensed



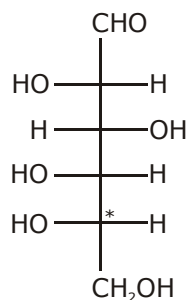
(ii) When  $\alpha\text{-NH}_2$  of both amino acids is used but in one terminal  $-\text{COOH}$  gp. lacking  $\alpha\text{-NH}_2$  gp. is used.



**15.** (a) The structure of L-glucose can be drawn by reversing the position of H and OH at the second last C-atom of D-glucose given i.e.,

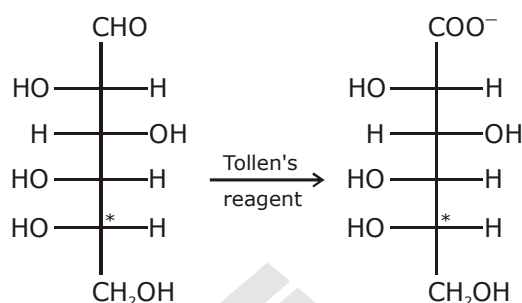


Hence structure of L-glucose will be :

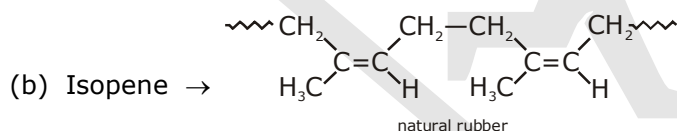
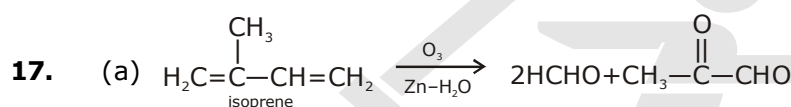


Position of H and OH at C\* is opposite to that in D.

(b) With Tollen's reagent the terminal  $-\text{CHO}$  group oxidised to  $-\text{COOH}$  group as :

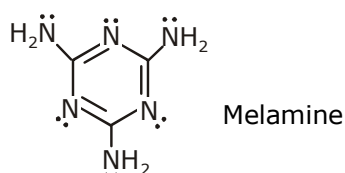


**16.** In structure (a), one ring has a free hemiacetal group, will hydrolyse into open chain in aqueous solution and therefore will reduce Tollen's reagent. Structure 'b' has only acetal groups, will not hydrolyse in aqueous solution into open chain, will not reduce Tollen's reagent.



**18.** 2      **19.** 8      **20.** 4

**21.** 0006



Lone pairs of electrons in malamine is 6.

**22.** 0004

Phe - Gly - Val - Ala  
Phe - Val - Gly - Ala  
Val - Gly - Phe - Ala  
Val - Phe - Gly - Ala  
(Glycine has no chiral centre)